# Boryl-Mediated Reversible $H_2$ Activation at Cobalt: Catalytic Hydrogenation, Dehydrogenation, and Transfer Hydrogenation

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SUPPORTING INFORMATION

**This PDF file includes:**

**Experimental procedures**

**Figure S1.** $^{1}H$, $^{11}B$, $^{13}C$, and $^{31}P$ NMR spectra of **2** under 1 atm $N_2$ at ambient temperature. $^{31}P$ NMR spectra at variable temperatures show that the broad resonance is not due to fluxional processes, and is likely the result of quadrupolar coupling with $^{59}Co$ (I = 7/2) and $^{11}B$ (I = 3/2).

**Figure S2.** $^{1}H$, $^{11}B$, $^{13}C$, and $^{31}P$ NMR spectra of **3** under 1 atm $H_2$ at ambient temperature.

**Figure S3.** $^{1}H$ NMR spectra of **3** under 1 atm $H_2$ at various temperatures.

**Figure S4.** $^{1}H$ NMR spectra of **3** under 4 atm $H_2$ at various temperatures.

**Figure S5.** $^{1}H$ NMR spectra of **3** under 4 atm HD at various temperatures.

**Figure S6.** $^{1}H$, $^{11}B$, $^{13}C$, and $^{31}P$ NMR spectra of **4** at ambient temperature.

**Figure S7.** $^{1}H$ (red) and $^{1}H\{^{11}B\}$ (green) NMR spectra of **4** at ambient temperature.

**Figure S8.** $^{1}H$-$^{1}H$ NOSEY spectrum of **4** at ambient temperature. Since no observable cross-peak exists between $H_a$ and $H_b$ (or $H_c$), the tentative assignments of $H_b$ and $H_c$ were made on the basis of our expectations of their relative chemical shifts owing to the presence or absence of a *trans* bridging hydride ligand. Since $H_b$ is *trans* to $H_a$, its resonance should be downfield from that of $H_c$ which is not *trans* to any ligand.

**Figure S9.** ATR-IR measured on a thin film of **1** under 1 atm $N_2$.

**Figure S10.** ATR-IR measured on a thin film of **2** under 1 atm $N_2$.

**Figure S11.** ATR-IR measured on a thin film of **3** under 1 atm $H_2$.

**Figure S12.** ATR-IR measured on a thin film of **4** under 1 atm $N_2$.

**Figure S13.** $^{1}H$ NMR spectra showing the conversion of **3** to **2** in toluene-$d_8$ at ambient temperature.

**Figure S14.** Solution IR spectra of **3** in *n*-pentane under a mixture of 1 atm $N_2/H_2$ (red) and 1 atm $N_2/D_2$ (blue). The inset shows the spectrum obtained by subtracting blue from red.

**Figure S15.** ATR-IR measured on a thin film of **3** under 1 atm $H_2$ (top). The conversion of **3** to **2** was accomplished by repeatedly dissolving/re-forming the thin film using $C_6D_6$ under 1 atm $N_2$.

**Figure S16.** (a) $^{1}H$ NMR spectrum of a mixture of **2** (2% mol), 1-octene, and hexamethylbenzene in $C_6D_6$ under 1 atm $N_2$ at ambient temperature. (b) $^{1}H$ NMR spectrum obtained three minutes after introducing 1 atm $H_2$. (c) $^{13}C$ NMR spectrum of the reaction mixture. (d) GC analysis of the reaction mixture (the retention time is identical to that of octane). (e) GC analysis of 1-octene.

**Figure S17.** (a) $^{1}H$ NMR spectrum of a mixture of **2** (2% mol) and styrene in $C_6D_6$ under 1 atm $N_2$ at ambient temperature. (b) $^{1}H$ NMR spectrum obtained three minutes after introducing 1 atm $H_2$. (c) $^{13}C$ NMR spectrum of the reaction mixture. (d) GC analysis of the reaction mixture (the retention time is identical to that of ethylbenzene). (e) GC analysis of styrene.

**Figure S18.** Top: $^{1}H$ NMR spectrum of **4** in $C_6D_6$ under 1 atm $N_2$ at ambient temperature. Bottom: $^{1}H$ NMR spectrum obtained after the addition of excess $Et_3N$.

**Figure S19.** Right: catalytic dehydrocoupling of $HMe_2N\text{-}BH_3$ monitored by $^{11}B$ and $^{11}B\{^{1}H\}$ NMR spectroscopies. The $BH_3$ resonance of $HMe_2NBH_2Me_2NBH_3$ at -13 ppm overlaps with that of $HNMe_2BH_3$. Left: Plot of molar ratio vs reaction time.

**Figure S20.** $^{1}H$ and $^{11}B$ NMR spectra showing catalytic transfer hydrogenation of styrene using $HMe_2N\text{-}BH_3$.

**Crystallographic Measurements**

**Figure S21.** Structure of **3** as determined crystallographically (left, two views) and optimized computationally (right, two views). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, except for the calculated Co-bound hydrides, are omitted for clarity.

**Computational Details**

**Table S1.** Selected bond lengths (Å) and angles (°) for complexes **2** and **4** as determined crystallographically and optimized computationally.

**Table S2.** Selected bond lengths (Å) and angles (°) for the four crystallographically independent molecules of complex **3** (donated as **3**, **3'**, **3''**, and **3'''**).

**Table S3.** Selected bond lengths (Å) and angles (°) for DFT-optimized isomers of complex **3**, namely boryl cobalt *trans*-dihydride dihydrogen (**A**), boryl cobalt *cis*-dihydride dihydrogen (**B**), dihydridoborato cobalt dihydrogen (**C**, the optimized structure is the same as **D**), and dihydridoborato cobalt dihydride (**D**).

**DFT optimized structural coordinates**

**General considerations.** Ligand **1** was prepared according to the reported procedures.[1] Solvents were dried by passing through an activated alumina column (*n*–pentane, benzene, $Et_2O$, and THF). Deuterated solvents were purchased from Cambridge Isotopes Laboratories, Inc. and were degassed and stored over activated 3 Å molecular sieves prior to use. $CoBr_2$, Na, Hg, and $HNMe_2$-$BH_3$ were purchased from Aldrich and used as received. Elemental analyses were performed by Midwest Microlab (Indianapolis, IN).

**Spectroscopic measurements.** Ambient temperature NMR spectra were recorded on a Varian 300 MHz, 400 MHz, and 500 MHz NMR spectrometers. Chemical shifts (δ) are given in ppm and are referenced against residual solvent signals ($^1$H, $^{13}$C) or external $BF_3$–$Et_2O$ ($^{11}$B) and $H_3PO_4$ ($^{31}$P). $T_1$(min) values were determined by fitting the pulse-recovery $^1$H spectra at various temperatures using the $T_1$ calculation protocols in either Varian's VnmrJ software or Mestrelab Research S. L.'s Mestrenova version 6.2.1. The ATR-IR measurements were obtained on a thin film of the complex obtained from evaporating a drop of the solution on the surface of a Bruker APLHA ATR-IR spectrometer probe (Platinum Sampling Module, diamond, OPUS software package) at 2 $cm^{-1}$resolution.

**Synthesis of 2.** To a THF solution (2 mL) of $CoBr_2$ (161 mg, 0.737 mmol) was added a THF solution (10 mL) of ligand **1** (160 mg, 0.368 mmol) at ambient temperature. After stirring for 30 min, the resulting solution was transferred to a THF suspension (10 mL) of freshly prepared sodium amalgam under $N_2$ atmosphere (Na: 33.9 mg, 1.473 mmol; Hg: 3.39 g). The mixture was allowed to stir at ambient temperature for 8 hours. The deep blue solution was decanted from mercury, and THF was removed under reduced pressure. The product was extracted into *n*-pentane (3 × 5 mL), and the solution was filtered through celite. Slow vapor diffusion into hexamethyldisiloxane afforded green crystals of **2** (45 mg, 23.5% based on **1**) which were isolated by filtration, washed with cold *n*-pentane, and dried under vacuum. $^1$H NMR (500 MHz; toluene-$d_8$): δ 1.27 (t, 36H, $^3J_{H-P}$ = 6.2 Hz), 3.73 (s, 4H), 6.87 (dd, 2H, $J_{H-H}$ = 5.6 Hz, $J_{H-H}$ = 3.2 Hz), 7.04 (dd, 2H, $J_{H-H}$ = 5.6 Hz, $J_{H-H}$ = 3.2 Hz). $^{13}$C{$^1$H} NMR (100 MHz; $C_6D_6$): δ 29.9 (t, $J_{C-P}$ = 2.6 Hz), 36.7 (t, $J_{C-P}$ = 4.1 Hz), 41.7 (bs), 108.2, 117.9, 139.5 (t, $J_{C-P}$ = 6.9 Hz). $^{11}$B{$^1$H} NMR (160 MHz; $C_6D_6$): δ 46.6. $^{31}$P{$^1$H} NMR (121 MHz; $C_6D_6$): δ 110.0 (bs). ATR-IR: $\nu_{N-N}$ = 2013 $cm^{-1}$. Elemental analysis calculated (%) for **2** ($C_{24}H_{44}BCoN_4P_2$): C, 55.40; H, 8.52; N, 10.77; found C, 55.53; H, 8.88; N, 7.00. *Note:* Combustion analysis was low in nitrogen in each of two independent attempts.

**Synthesis of 3.** *Method A* (*in situ* generation): A J. Young NMR tube containing a toluene-$d_8$ solution of **2** was subjected to one freeze-pump-thaw cycle and then back filled with 1 atm $H_2$. Quantitative formation of **3** was observed immediately by multinuclear NMR spectroscopies. *Method B*: Complex **2** (20 mg) was dissolved in 5 mL *n*-pentane under 1 atm $H_2$. Slow solvent evaporation under dihydrogen atmosphere afforded greenish yellow crystals of **3** (8 mg) suitable for X-ray crystallographic analysis. $^1$H NMR (500 MHz; toluene-$d_8$): δ −6.51 (bs, 4H), 1.12 (t, 36H, $^3J_{H-P}$ = 6.0 Hz), 3.47 (s, 4H), 6.74 (dd, 2H, $J_{H-H}$ = 5.5 Hz, $J_{H-H}$ = 3.2 Hz), 7.01 (dd, 2H, $J_{H-H}$ = 5.5 Hz, $J_{H-H}$ = 3.2 Hz). $^{13}$C{$^1$H} NMR (100 MHz; $C_6D_6$): δ 29.3 (t, $J_{C-P}$ = 2.4 Hz), 34.3 (t, $J_{C-P}$ = 4.6 Hz), 40.6 (t, $J_{C-P}$ = 13.7 Hz), 106.6, 117.3, 141.3 (t, $J_{C-P}$ = 6.3 Hz). $^{11}$B{$^1$H} NMR (160 MHz; $C_6D_6$): δ 47.1. $^{31}$P{$^1$H} NMR (121 MHz;

$C_6D_6$): δ 138.2. ATR-IR: $\nu_{Co\text{-}H/B\text{-}H}$ = 1836 $cm^{-1}$. *Note:* Satisfactory combustion analysis for **3** was not obtained, presumably due to the lability of $H_2$ in the presence of $N_2$.

**Synthesis of 4.** To a pentane solution (5 mL) of **2** (20 mg, 0.038 mmol) was added solid $HMe_2N\text{-}BH_3$ (5.0 mg, 0.085 mmol) in one portion at ambient temperature, leading to an immediate color change from blue to brown. The resulting solution was allowed to stir for 10 min. Slow solvent evaporation under $N_2$ atmosphere afforded dark brown crystals of **4** (16 mg, 82%), which was collected by filtration, washed with cold *n*-pentane, and dried under vacuum. $^1$H NMR (400 MHz; $C_6D_6$): δ -27.70 (t, 1H, B-*H*-Co, $^2J_{H-P}$ = 40 Hz), -14.11 (bs, 1H, Co-$H_2BH_2$), -0.77 (bs, 1H, Co-$H_2BH_2$), 1.19 (t, 18H, $^3J_{H-P}$ = 6.1 Hz), 1.22 (t, 18H, $^3J_{H-P}$ = 6.1 Hz), 3.27 (d, 2H, $^2J_{H\text{-}H}$ = 11.3 Hz), 3.52 (d, 2H, $^2J_{H\text{-}H}$ = 11.3 Hz), 4.36 (bs, 2H, Co-$H_2BH_2$), 6.79 (dd, 2H, $J_{H\text{-}H}$ = 5.5 Hz, $J_{H\text{-}H}$ = 3.3 Hz), 7.06 (dd, 2H, $J_{H\text{-}H}$ = 5.5 Hz, $J_{H\text{-}H}$ = 3.3 Hz). $^{13}$C{$^1$H} NMR (100 MHz; $C_6D_6$): δ 29.4 (t, $J_{C\text{-}P}$ = 1.6 Hz), 29.7 (t, $J_{C\text{-}P}$ = 1.6 Hz), 35.1 (t, $J_{C\text{-}P}$ = 4.3 Hz), 35.6 (t, $J_{C\text{-}P}$ = 4.3 Hz), 40.1 (t, $J_{C\text{-}P}$ = 17.5 Hz), 107.5, 118.0, 140.8 (t, $J_{C\text{-}P}$ = 6.3 Hz). $^{11}$B{$^1$H} NMR (160 MHz; $C_6D_6$): δ 5.7 (1B, Co-$H_2BH_2$), 40.4 (1B, *B*-H-Co). $^{31}$P{$^1$H} NMR (121 MHz; $C_6D_6$): δ 103.3 (bs). ATR-IR: $\nu_{B\text{-}H}$ = 2422, 2342, 1959, 1901, and 1786 $cm^{-1}$. Elemental analysis calculated (%) for **4** ($C_{24}H_{49}B_2CoN_2P_2$): C, 56.73; H, 9.72; N, 5.51; found C, 56.31; H, 9.57; N, 5.37.

**Variable temperature NMR experiments under $H_2$ or HD atmosphere.** A sample of **2** (6 mg) dissolved in toluene-$d_8$ in a J. Young tube was subjected to one freeze–pump–thaw cycle, then exposed to $H_2$ or HD (generated from the reaction of excess $LiAlH_4$ and $D_2O$). For a higher pressure, the entire NMR tube was cooled with liquid nitrogen under vacuum and then back filled with $H_2$ or HD (1 atm), leading to a pressure of 4 atm after the sealed tube warmed to ambient temperature.

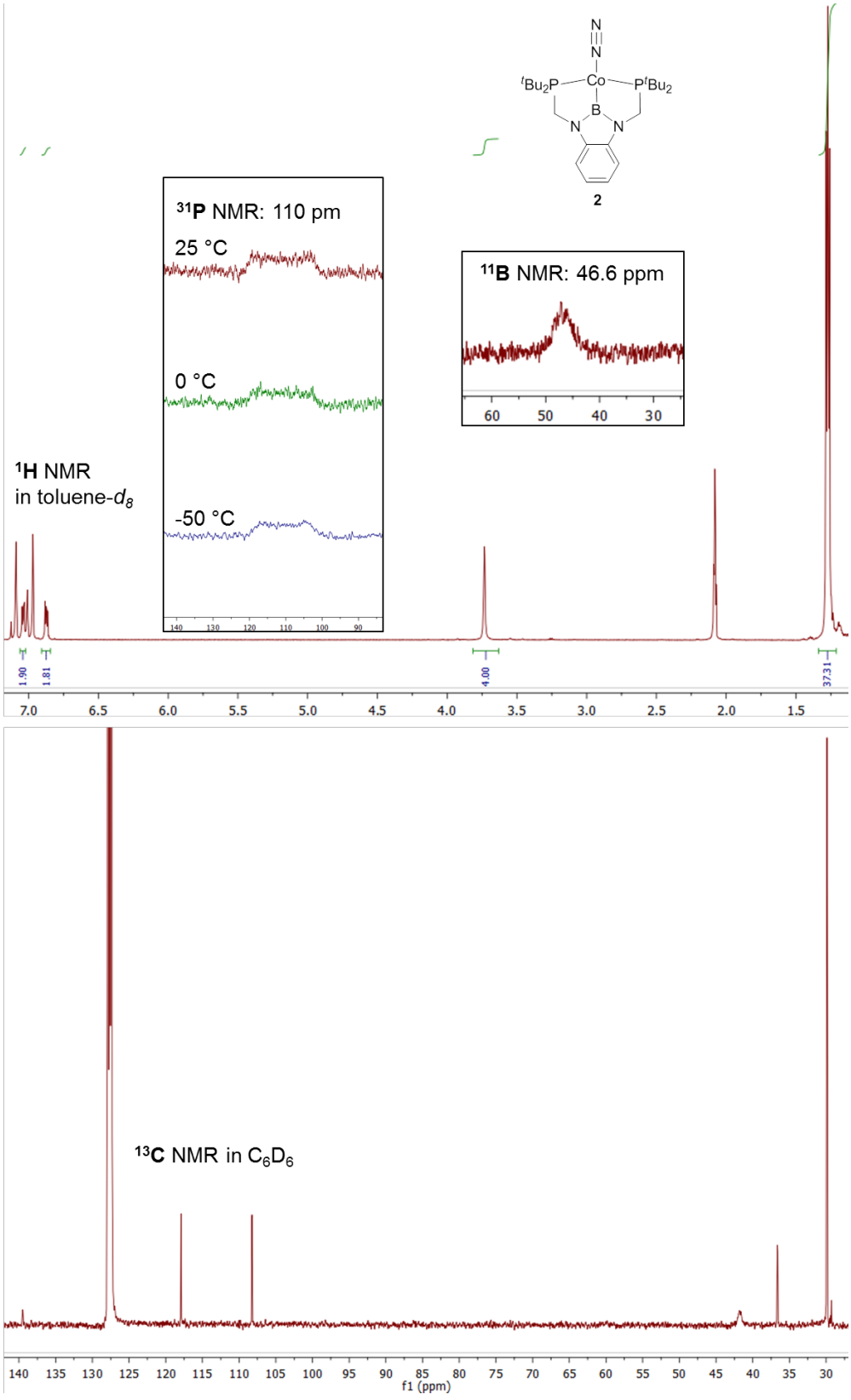



**Figure S1.** $^{1}H$, $^{11}B$, $^{13}C$, and $^{31}P$ NMR spectra of **2** under 1 atm $N_2$ at ambient temperature. $^{31}P$ NMR spectra at variable temperatures show that the broad resonance is not due to fluxional processes, and is likely the result of quadrupolar coupling with $^{59}Co$ (I = 7/2) and $^{11}B$ (I = 3/2).

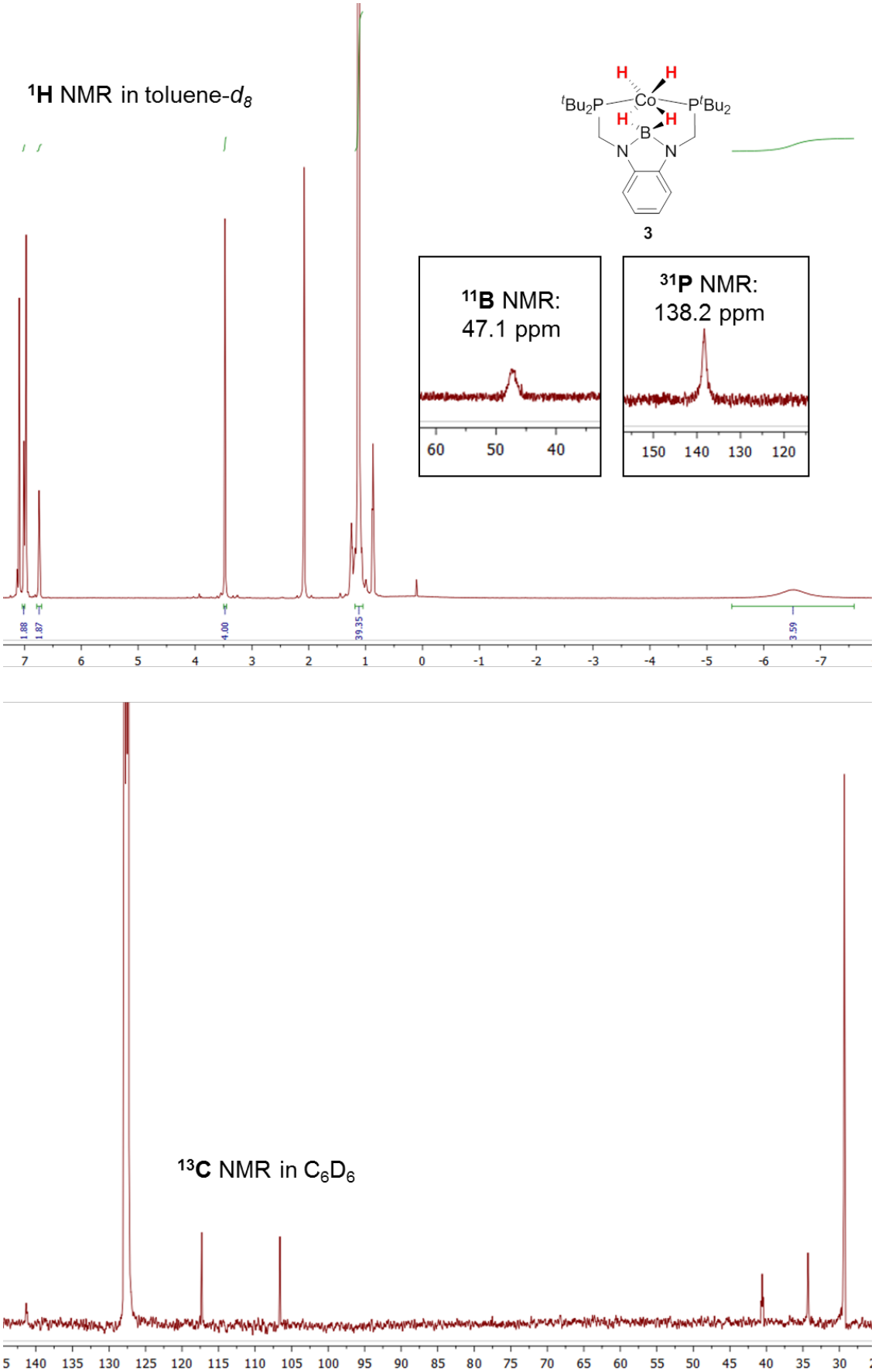



**Figure S2.** $^{1}H$, $^{11}B$, $^{13}C$, and $^{31}P$ NMR spectra of **3** under 1 atm $H_2$ at ambient temperature.

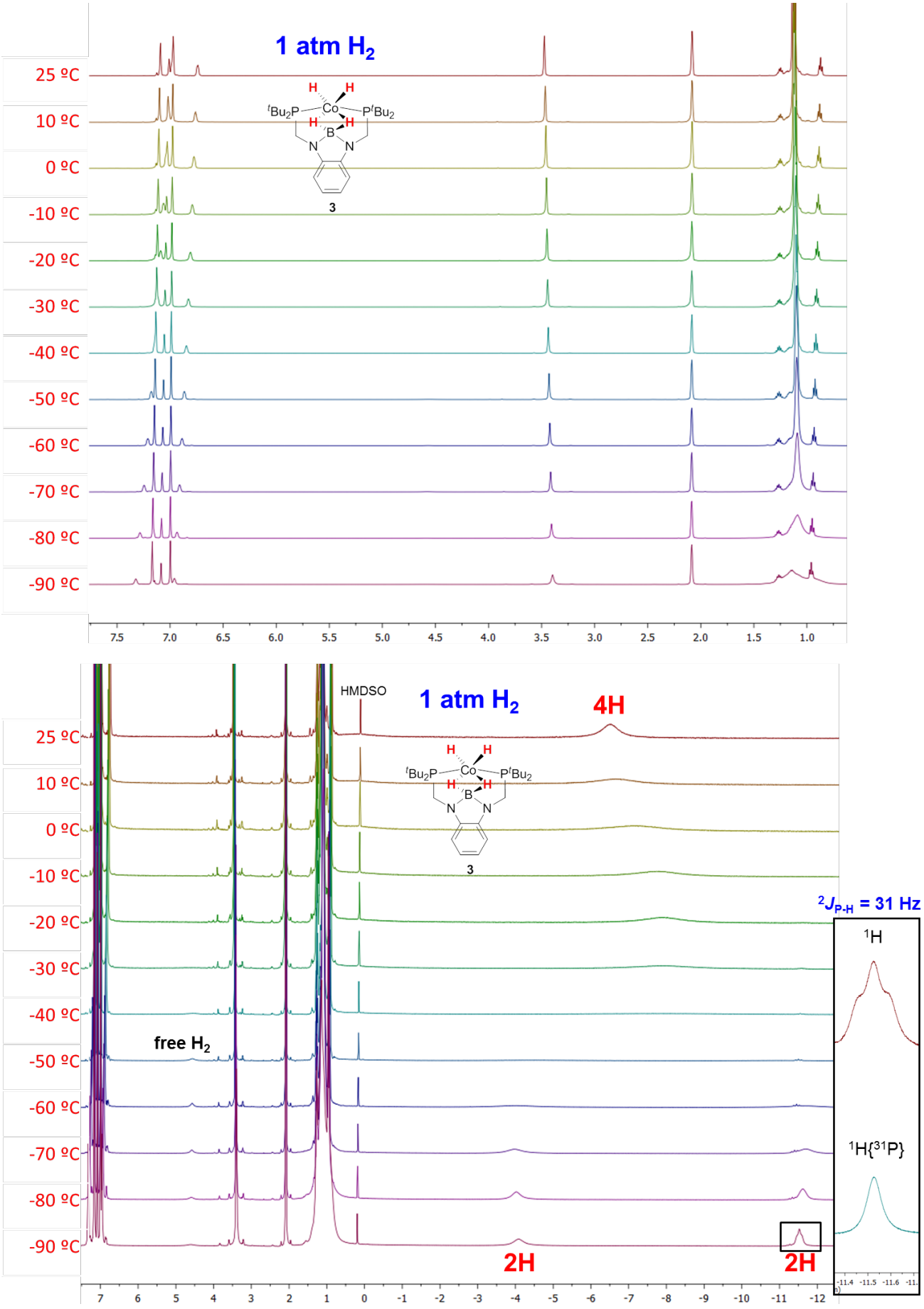



**Figure S3.** $^{1}$H NMR spectra of **3** under 1 atm $H_2$ at various temperatures.

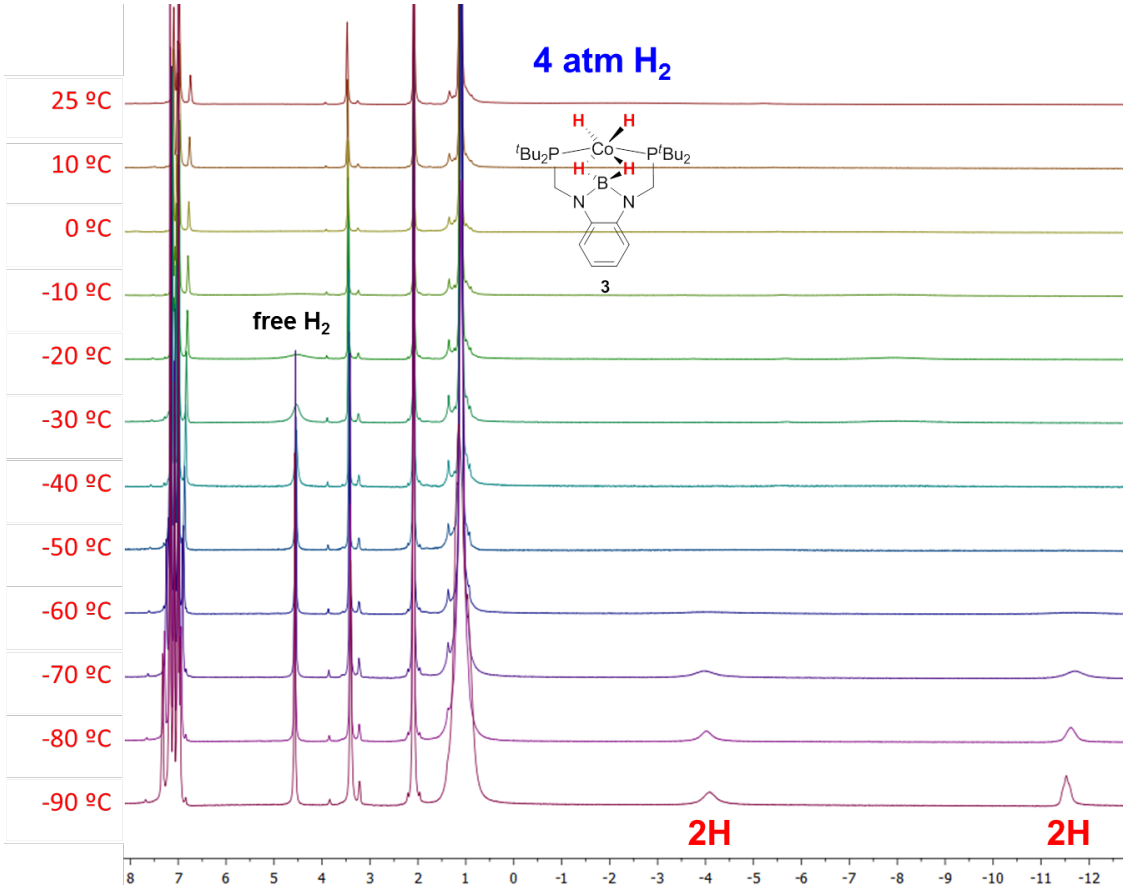



**Figure S4.** $^1$H NMR spectra of **3** under 4 atm $H_2$ at various temperatures.

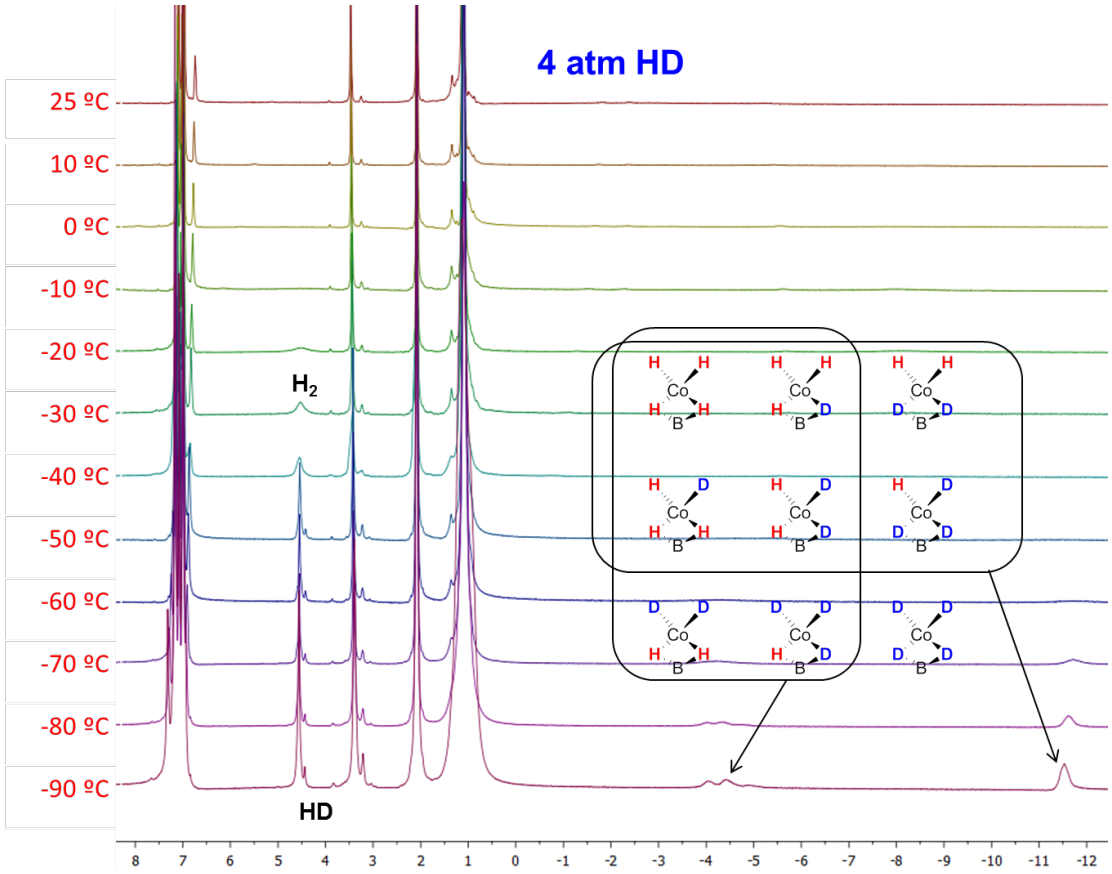



**Figure S5.** $^1$H NMR spectra of **3** under 4 atm HD at various temperatures.

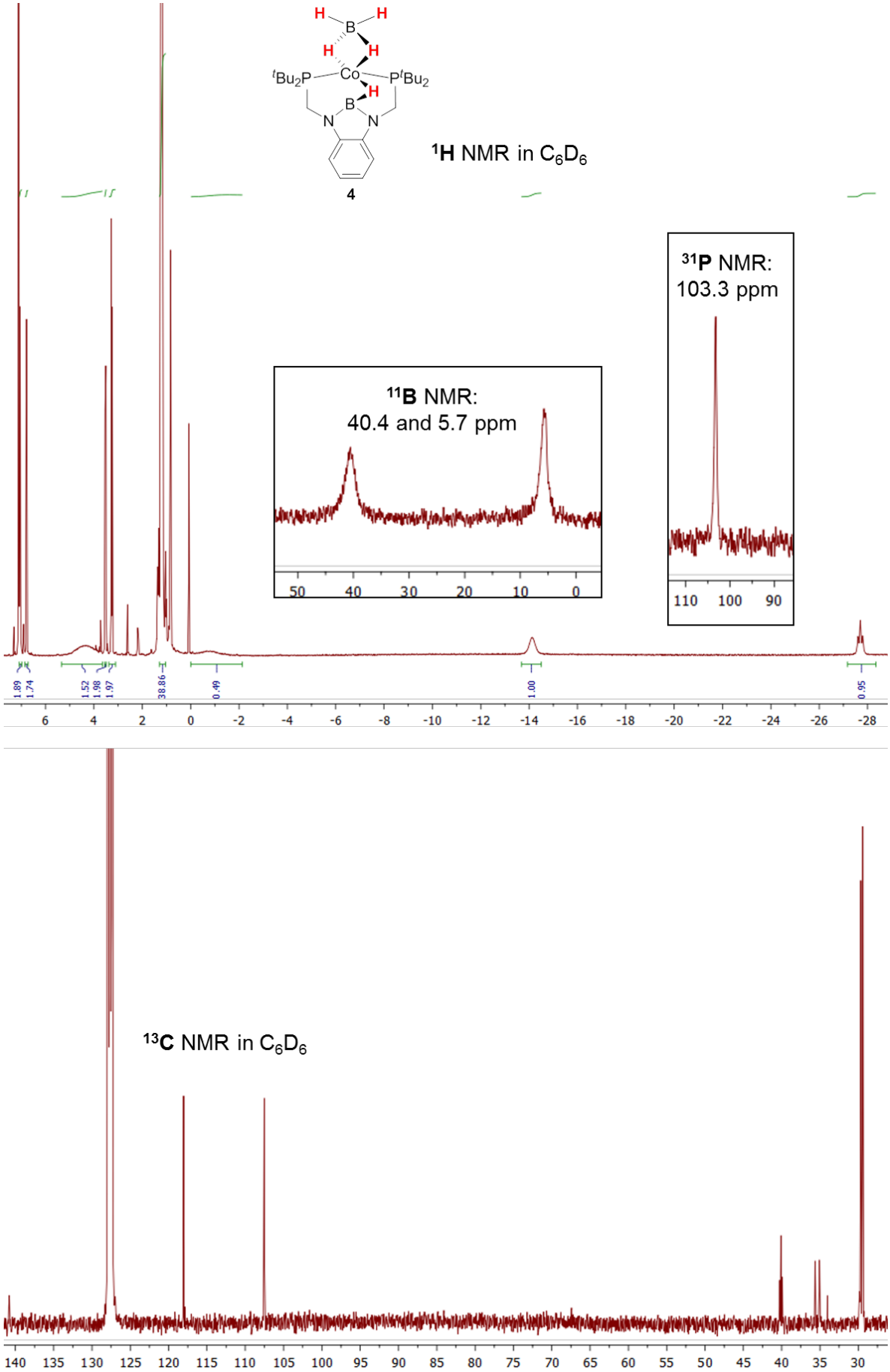



**Figure S6.** $^{1}$H, $^{11}$B, $^{13}$C, and $^{31}$P NMR spectra of **4** at ambient temperature.

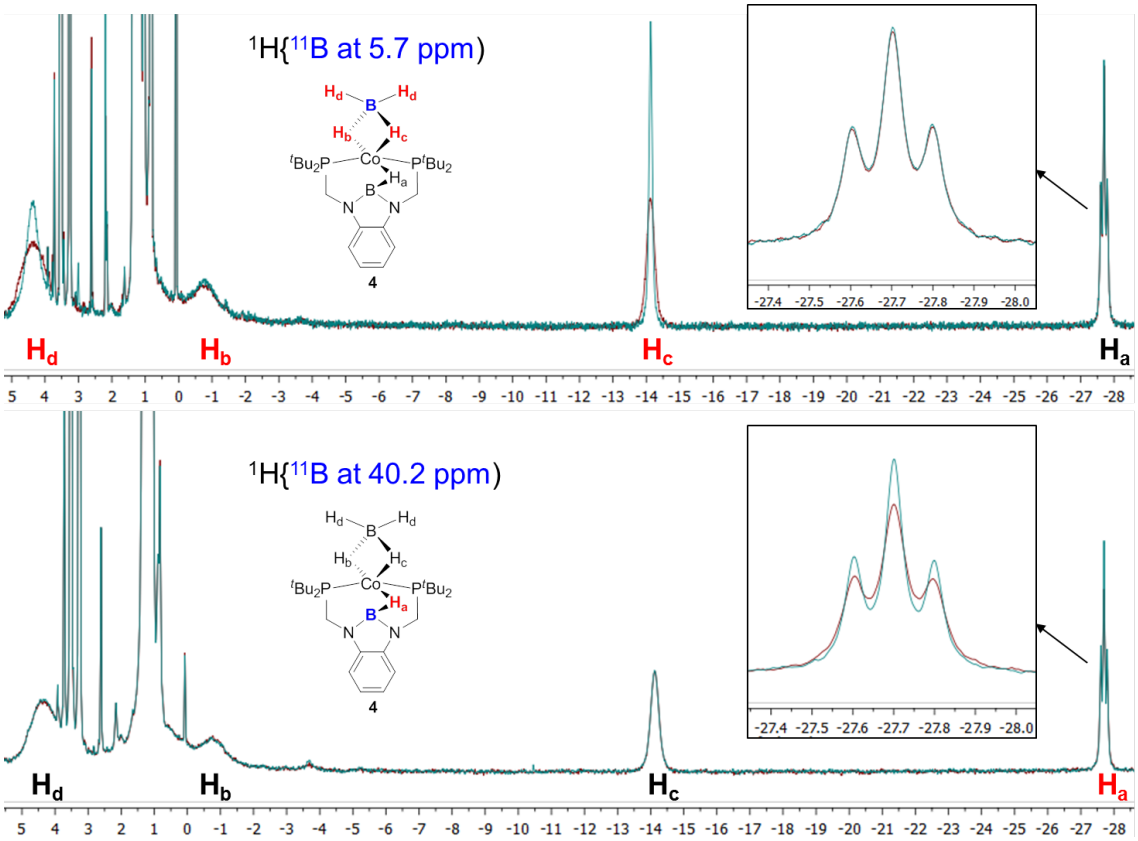



**Figure S7.** $^1$H (red) and $^1$H{$^{11}$B} (green) NMR spectra of **4** at ambient temperature.

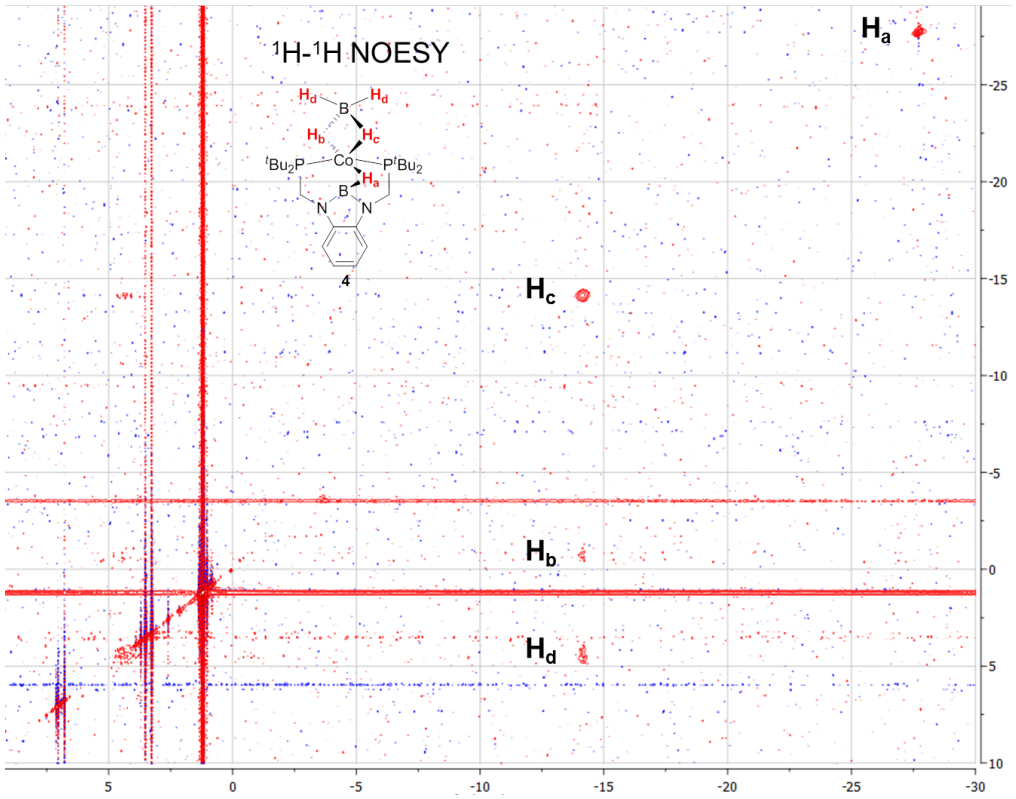



**Figure S8.** $^1$H-$^1$H NOESY spectrum of **4** at ambient temperature. Since no observable cross-peak exists between $H_a$ and $H_b$ (or $H_c$), the tentative assignments of $H_b$ and $H_c$ were made on the basis of our expectations of their relative chemical shifts owing to the presence or absence of a *trans* bridging hydride ligand. Since $H_b$ is *trans* to $H_a$, its resonance should be downfield from that of $H_c$ which is not *trans* to any ligand.

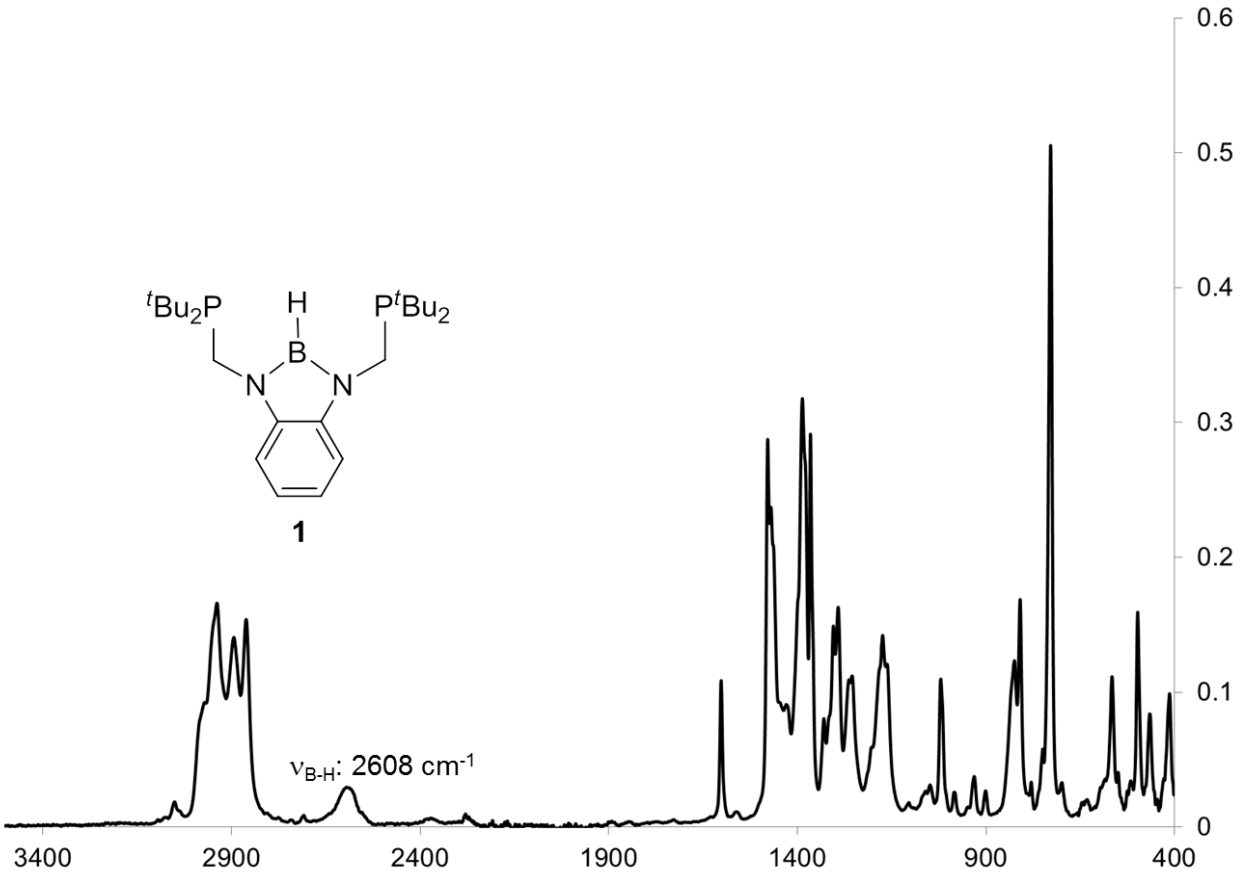



**Figure S9.** ATR-IR measured on a thin film of **1** under 1 atm $N_2$.

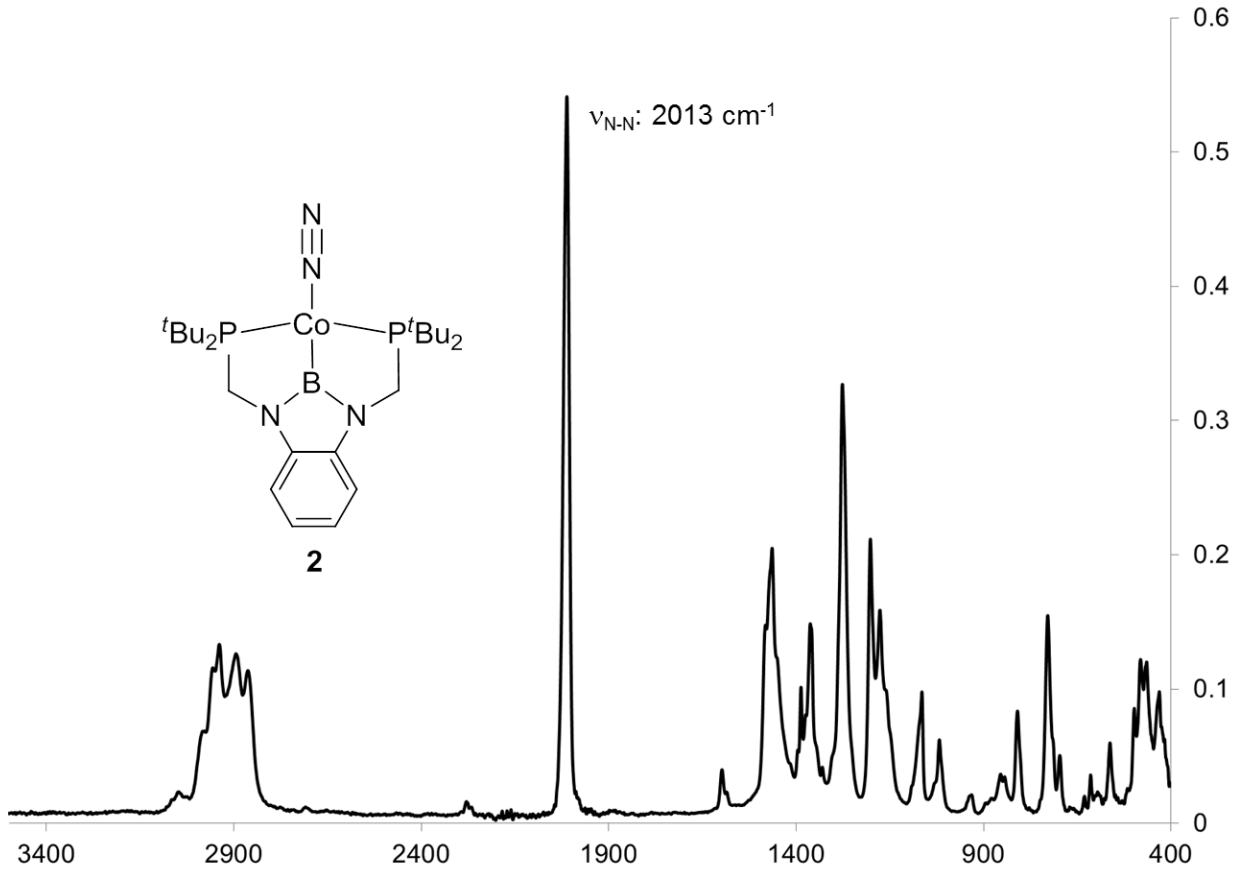



**Figure S10.** ATR-IR measured on a thin film of **2** under 1 atm $N_2$.

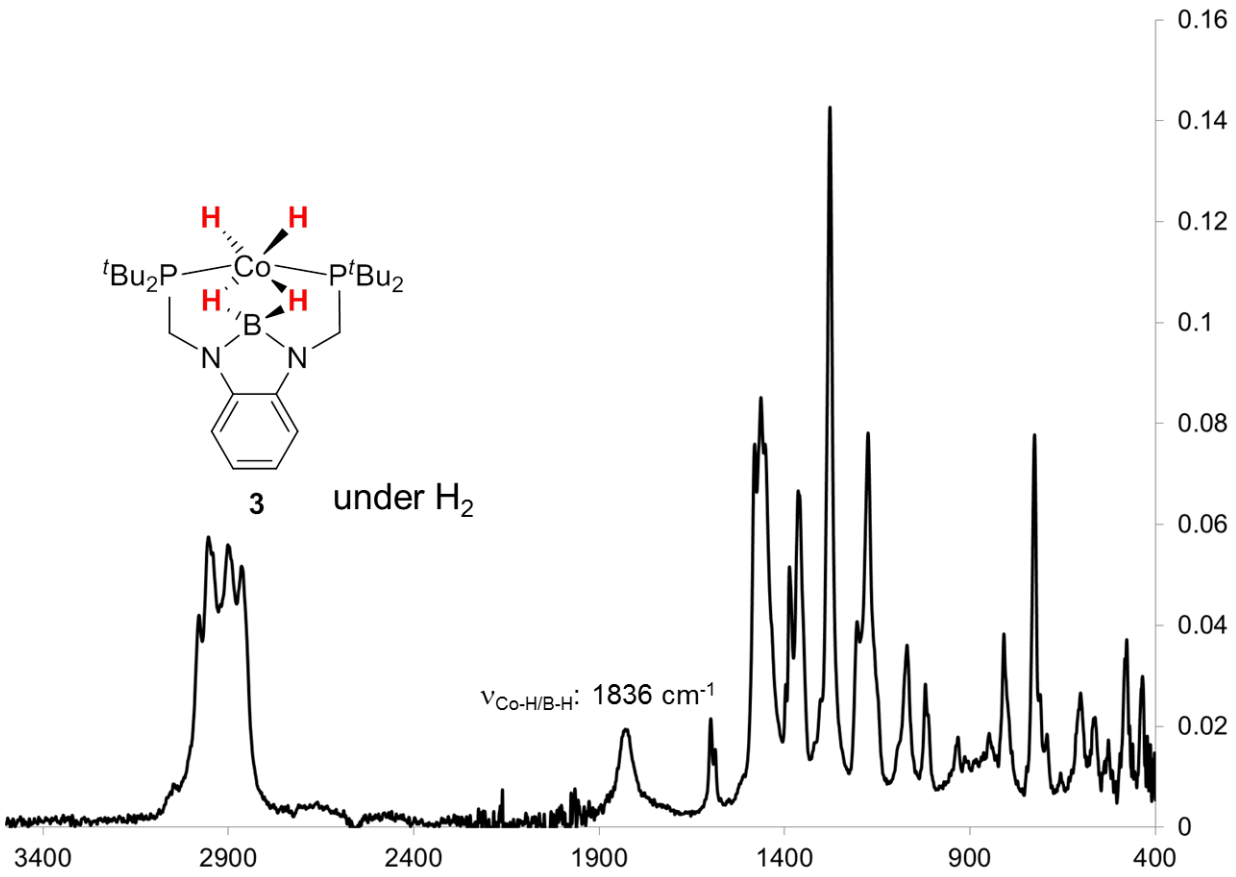



**Figure S11.** ATR-IR measured on a thin film of **3** under 1 atm $H_2$.

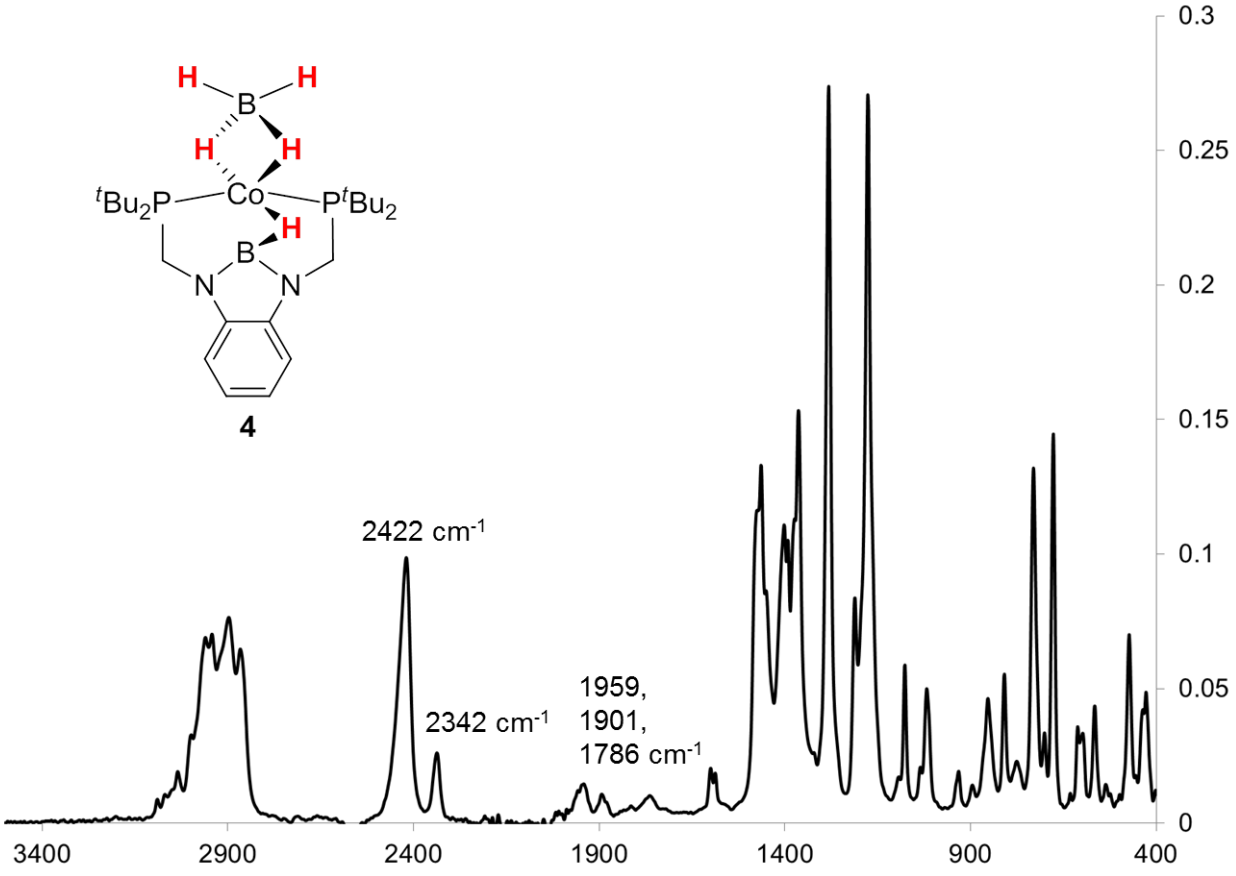



**Figure S12.** ATR-IR measured on a thin film of **4** under 1 atm $N_2$.

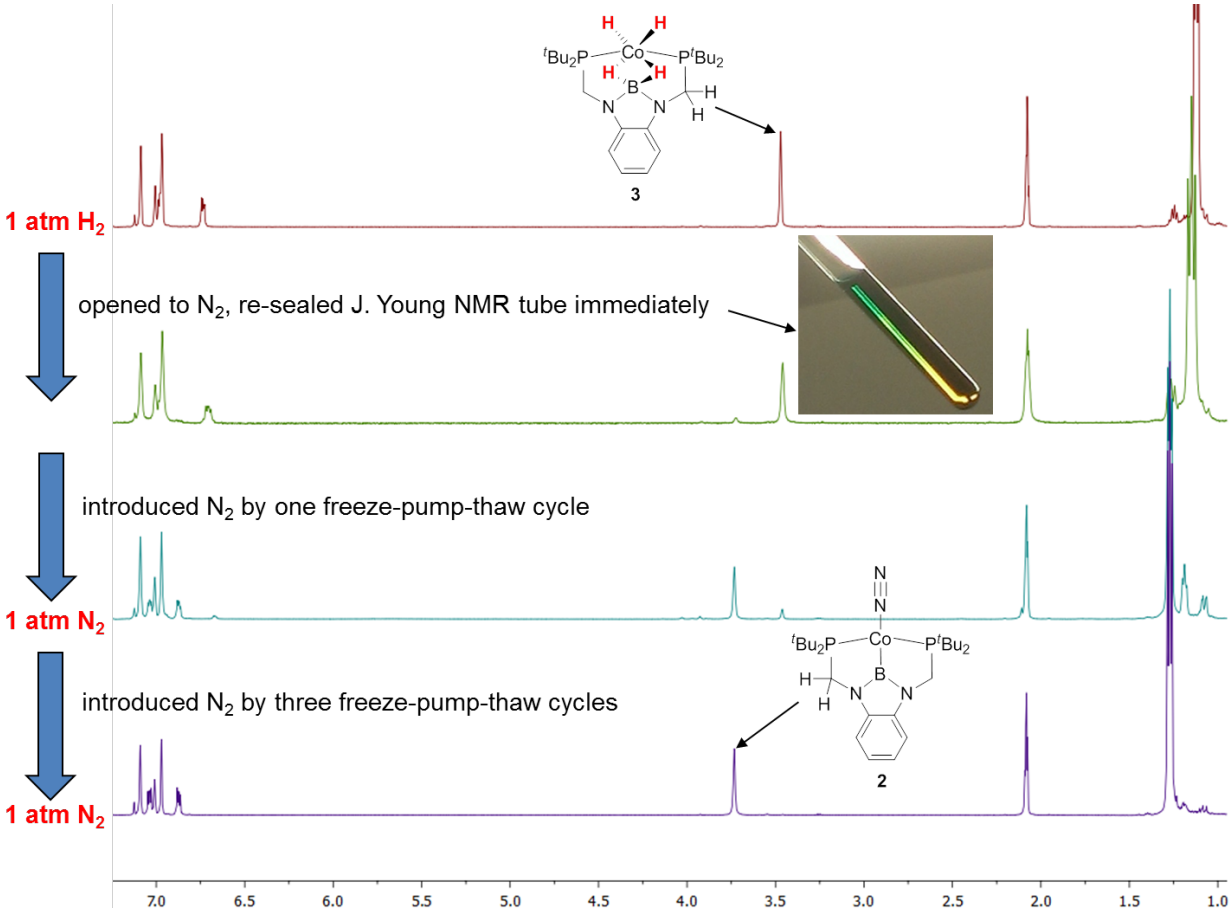



**Figure S13.** $^1$H NMR spectra showing the conversion of **3** to **2** in toluene-$d_8$ at ambient temperature.

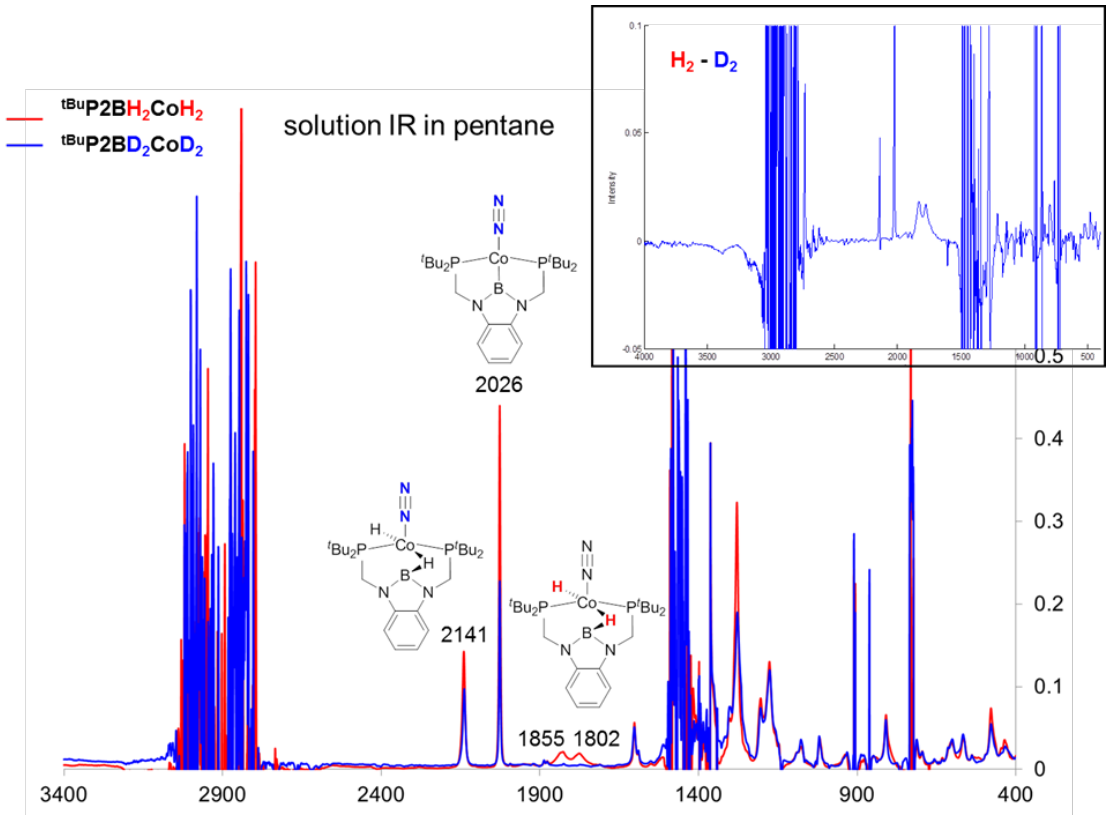



**Figure S14.** Solution IR spectra of **3** in *n*-pentane under a mixture of 1 atm $N_2/H_2$ (red) and 1 atm $N_2/D_2$ (blue). The inset shows the spectrum obtained by subtracting blue from red.

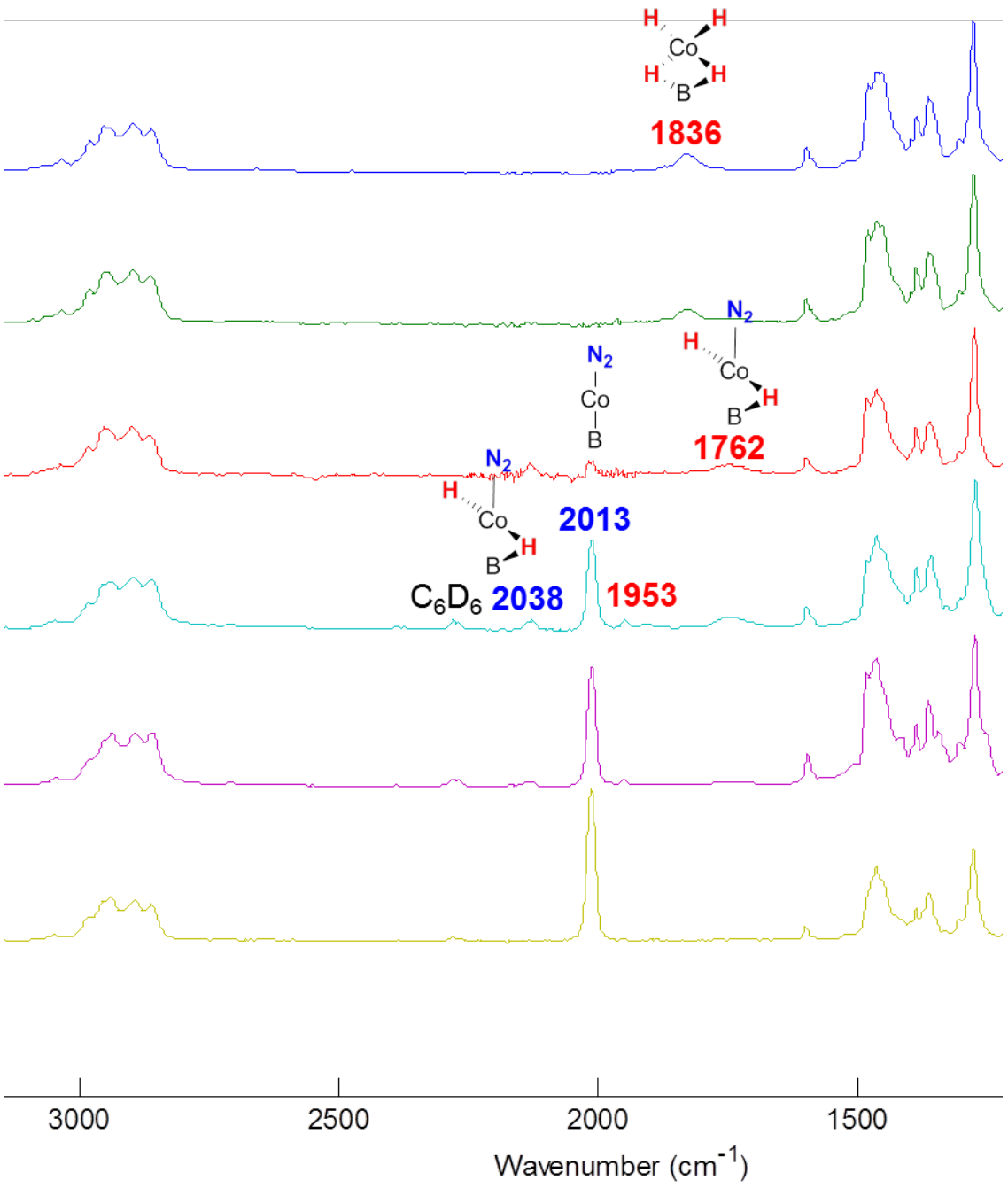



**Figure S15.** ATR-IR measured on a thin film of **3** under 1 atm $H_2$ (top). The conversion of **3** to **2** was accomplished by repeatedly dissolving/re-forming the thin film using $C_6D_6$ under 1 atm $N_2$.

**Catalytic hydrogenation of olefins.** A J. Young NMR tube was charged with **2** (2% mol), olefins, and hexamethylbenzene (an internal standard) in $C_6D_6$. The tube was subjected to one freeze-pump-thaw cycle on a high-vacuum line. After back filling the tube with 1 atm $H_2$, the tube was immediately sealed, frozen with liquid nitrogen, and brought to the spectrometer. Upon thawing, the color changed from blue to yellow in a period of 180 sec. The reaction was then monitored by $^1H$ and $^{13}C$ NMR spectroscopies as well as GC analyses. Control experiments carried out under the same conditions in the presence of Hg showed similar results. Control experiments carried out in the absence of **2** indicated no reactivity. Catalytic styrene hydrogenation by $(PPh_3)_3RhCl$ was carried out under the same conditions in THF-$d_8$/$C_6D_6$ (50/50). A full conversion of styrene to ethylbenzene was accomplished in 30 min, corresponding to a TOF of 100/hour.

**Catalytic dehydrogenation of $HMe_2N$-$BH_3$.** Complex **2** (or **4**, 2% mol) and $HMe_2N$-$BH_3$ were mixed in $C_6D_6$ (10 mL) and transferred to a Schlenk tube. The mixture was allowed to stir at ambient temperature under 1 atm $N_2$. The color of the solution remained brown during the catalysis. To monitor the progress of the reaction, a small portion (~0.1 mL) of the mixture was transferred to a vial, diluted with $C_6D_6$, and quenched by filtering through silica gel under air. The resulting solution was monitored by $^{11}B$ NMR spectroscopy, and the identities of the products were assigned according to the literature.[2] Control experiments carried out under the same conditions in the presence of Hg showed similar results. Control experiments carried out in the absence of **2** indicated no reactivity.

**Catalytic hydrogenation of styrene using $HMe_2N$-$BH_3$ as a hydrogen source.** Complex **2** (0.02 mmol), styrene (1.0 mmol), and $HMe_2N$-$BH_3$ (1.0 mmol) were mixed in $C_6D_6$ (5 mL) under 1 atm $N_2$. The mixture was subjected to a 10-fold dilution and transferred to a J. Young NMR tube under $N_2$ atmosphere, allowing the reaction to be monitored by $^1H$ NMR spectroscopy. The color of the solution remained brown during the catalysis. In order to achieve stirring, the tube was rotated at 10-15 rpm when spectra were not being collected. Control experiments carried out under the same conditions in the presence of Hg showed similar results. Control experiments carried out in the absence of **2** indicated no reactivity after stirring for 24 hours.

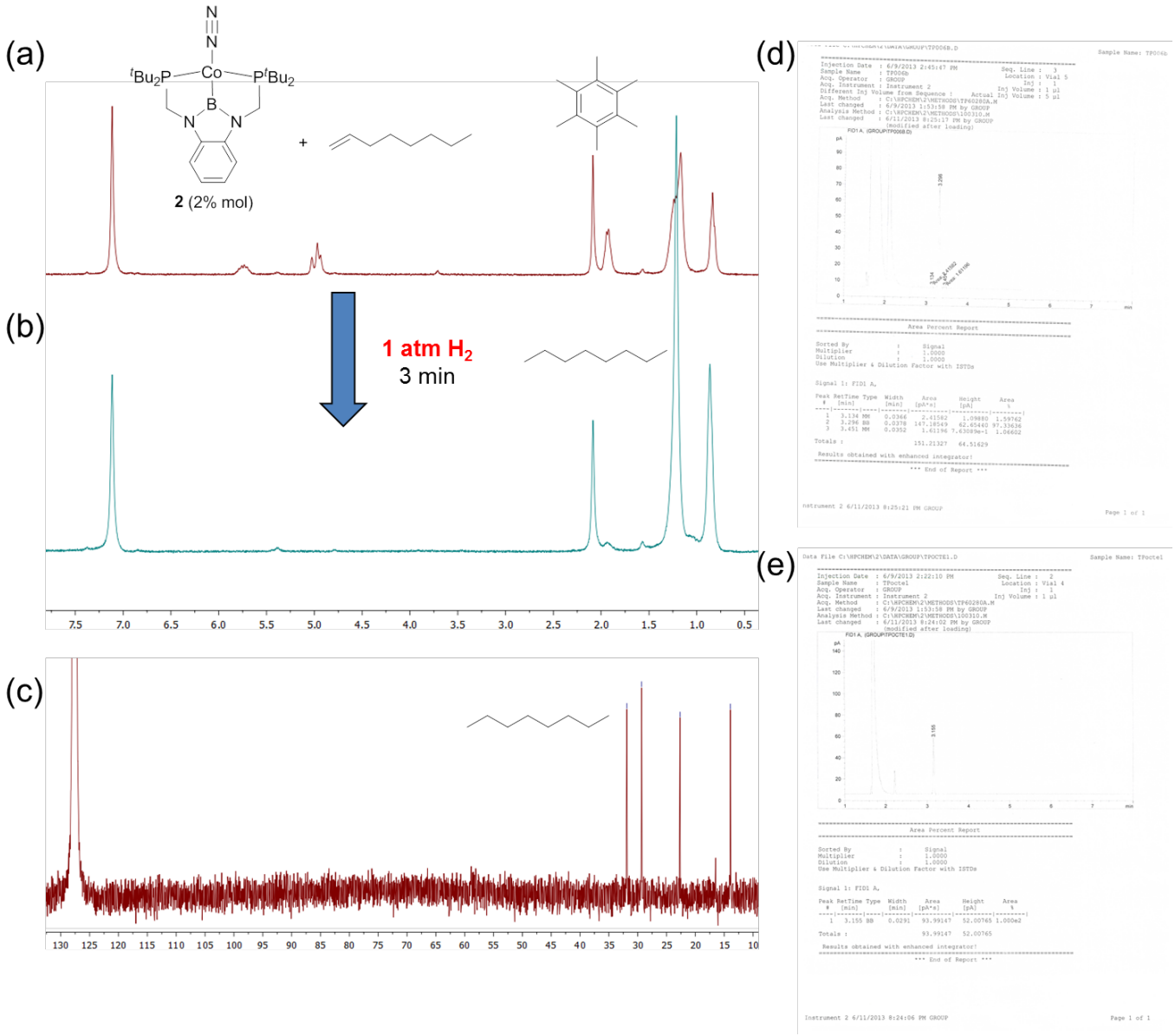



**Figure S16.** (a) $^{1}$H NMR spectrum of a mixture of **2** (2% mol), 1-octene, and hexamethylbenzene in $C_6D_6$ under 1 atm $N_2$ at ambient temperature. (b) $^{1}$H NMR spectrum obtained three minutes after introducing 1 atm $H_2$. (c) $^{13}$C NMR spectrum of the reaction mixture. (d) GC analysis of the reaction mixture (the retention time is identical to that of octane). (e) GC analysis of 1-octene.

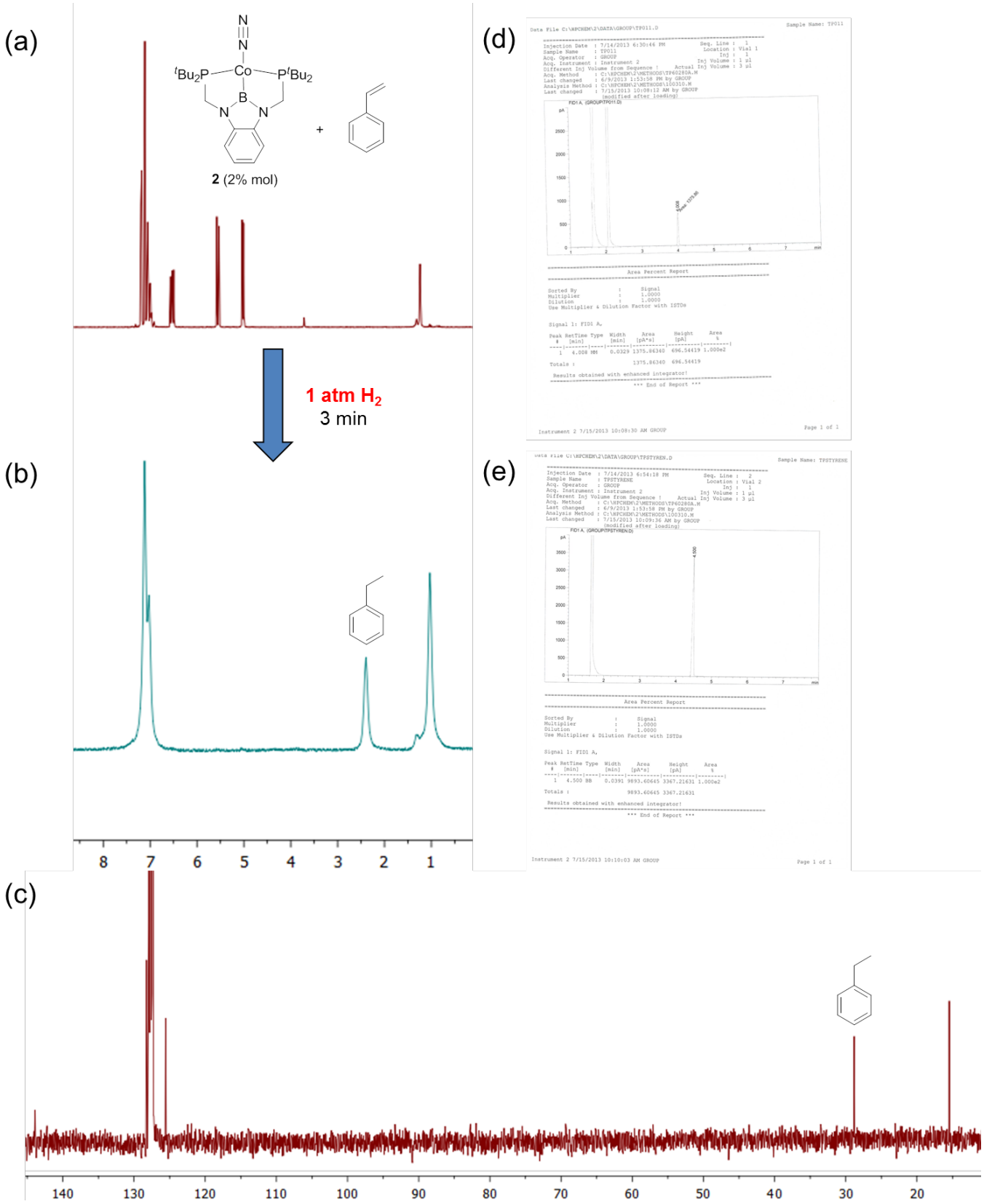



**Figure S17.** (a) $^{1}$H NMR spectrum of a mixture of **2** (2% mol) and styrene in $C_6D_6$ under 1 atm $N_2$ at ambient temperature. (b) $^{1}$H NMR spectrum obtained three minutes after introducing 1 atm $H_2$. (c) $^{13}$C NMR spectrum of the reaction mixture. (d) GC analysis of the reaction mixture (the retention time is identical to that of ethylbenzene). (e) GC analysis of styrene.

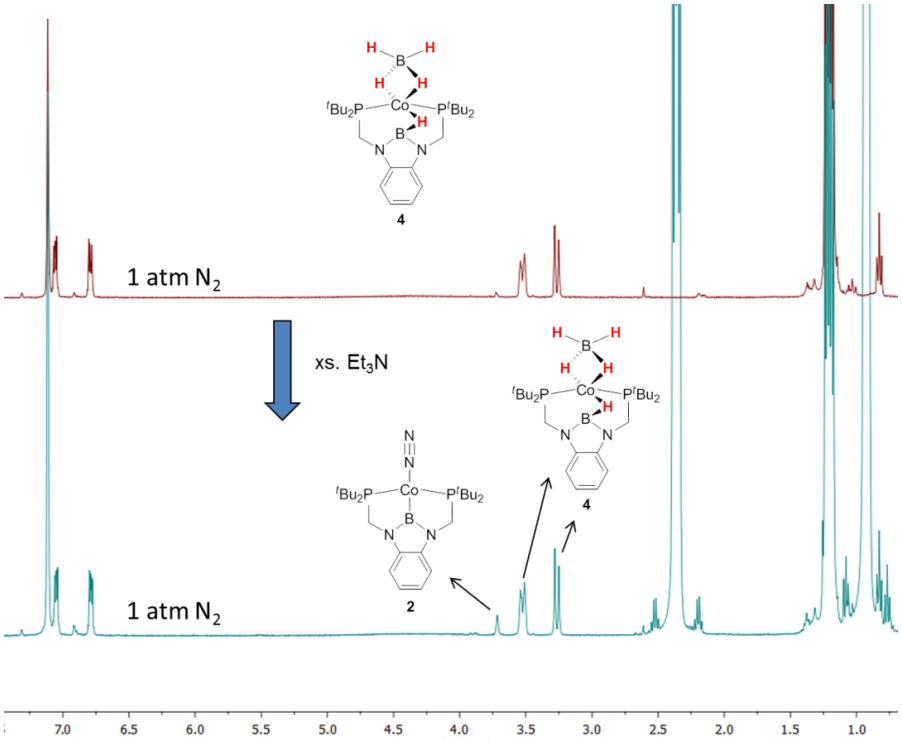



**Figure S18.** Top: $^{1}H$ NMR spectrum of **4** in $C_6D_6$ under 1 atm $N_2$ at ambient temperature. Bottom: $^{1}H$ NMR spectrum obtained after the addition of excess $Et_3N$.

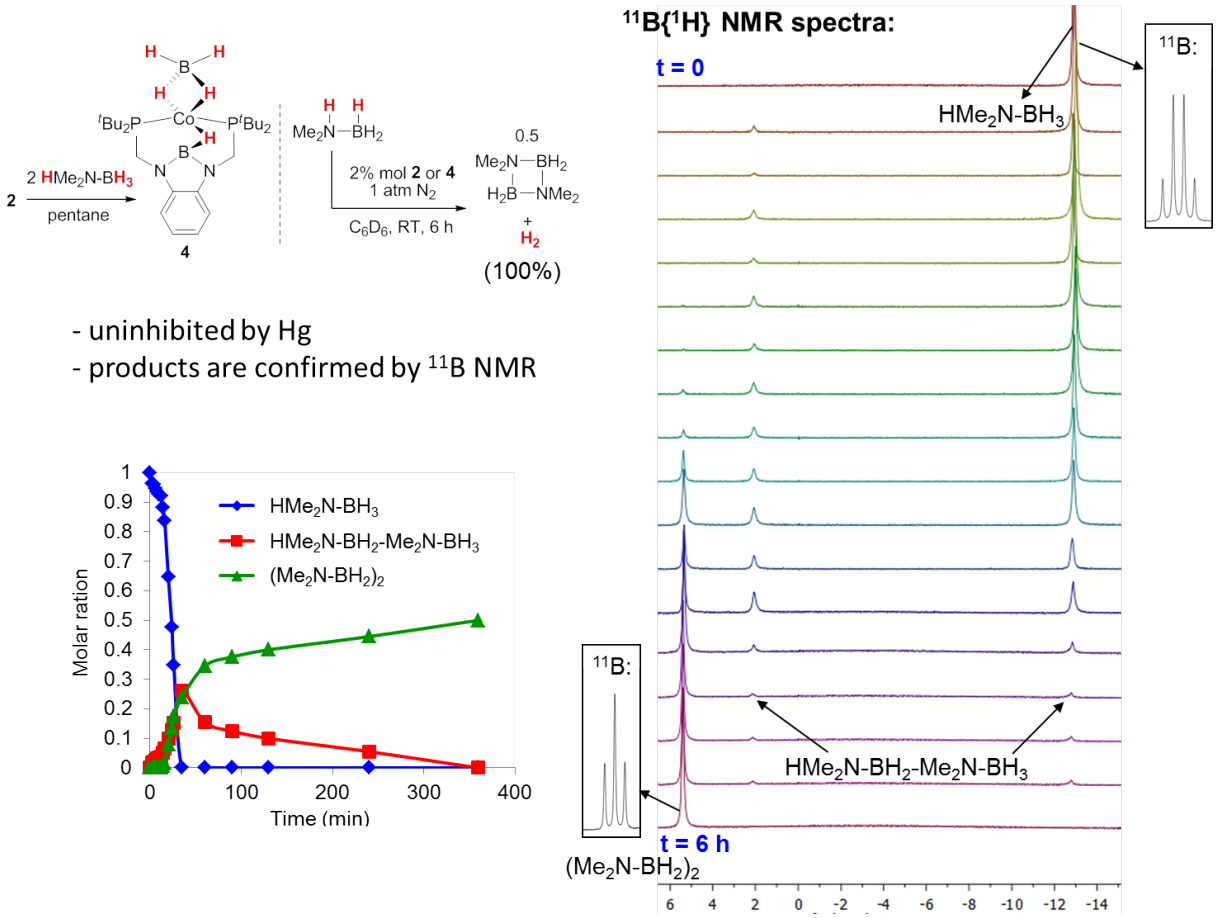



**Figure S19.** Right: catalytic dehydrocoupling of $HMe_2N$-$BH_3$ monitored by $^{11}B$ and $^{11}B\{^{1}H\}$ NMR spectroscopies. The $BH_3$ resonance of $HMe_2NBH_2Me_2NBH_3$ at -13 ppm overlaps with that of $HNMe_2BH_3$. Left: Plot of molar ratio vs reaction time.

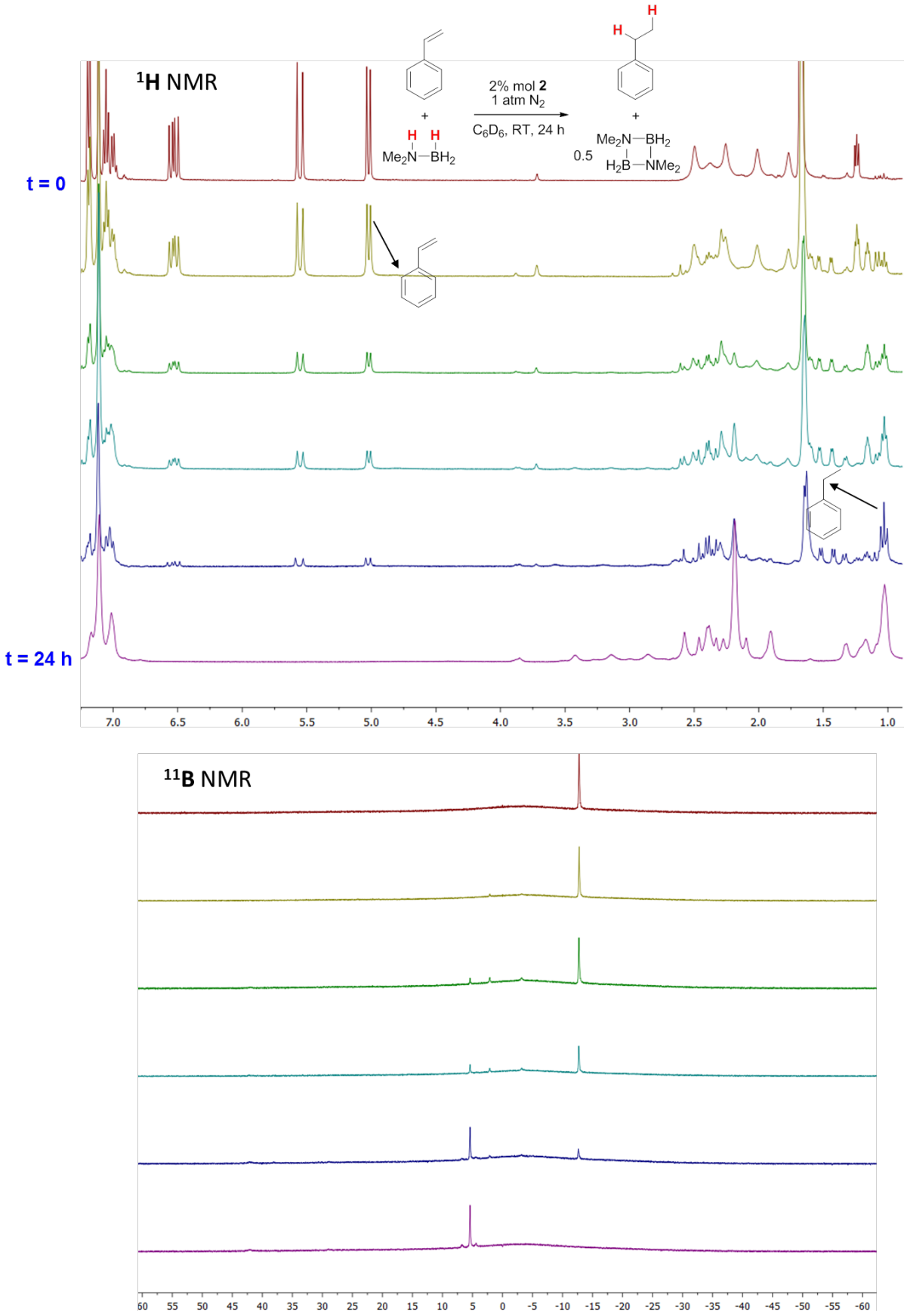



**Figure S20.** $^{1}H$ and $^{11}B$ NMR spectra showing catalytic transfer hydrogenation of styrene using $HMe_2N$-$BH_3$.

**Crystallographic Measurements.** The crystallographic measurements were performed at 100(2) K using a Bruker APEX–II CCD area detector diffractometer (Mo-$K_\alpha$ radiation, $\lambda = 0.71073$ Å). In each case, a specimen of suitable size and quality was selected and mounted onto a nylon loop. The structures were solved by direct methods, which successfully located most of the nonhydrogen atoms. Semi–empirical absorption corrections were applied.[3] Subsequent refinement on $F^2$ using the SHELXTL/PC package (version 6.1) allowed location of the remaining non–hydrogen atoms.[4]

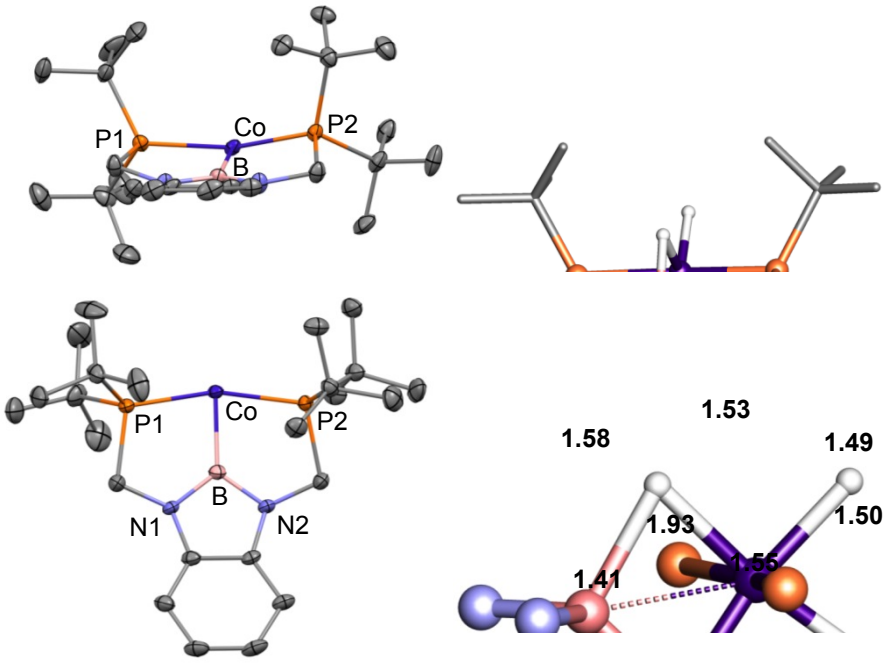



**Figure S21.** Structure of **3** as determined crystallographically (left, two views) and optimized computationally (right, two views). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, except for the calculated Co-bound hydrides, are omitted for clarity.

**Computational Details.** Density functional theory (DFT) structural optimizations were performed on the solid-state structures (**2** and **4**) without any symmetry restraints using Gaussian 03 suite of programs[5] with BP86 functional[6] and a 6-31+G(d,p) basis set on all atoms. To model the isomers **A** and **B**, hydride ligands were placed *trans* or *cis* to each other at 1.5 Å from cobalt. The H atoms of the dihydrogen ligand were placed at a distance of 1.5 Å from cobalt and 0.85 Å from each other. To model isomer **C**, bridging hydride ligands were placed at 1.5 Å from cobalt and boron. The H atoms of the dihydrogen ligand were placed *trans* to boron at a distance of 1.5 Å from cobalt and 0.85 Å from each other. The starting geometry of isomer **D** contains four hydride ligands which occupy the equatorial plane of a pseudo-octahedral cobalt center. Bridging hydrides were placed at 1.5 Å from cobalt and boron, and terminal hydrides were placed at a distance of 1.5 Å from cobalt. Frequency calculations performed on the optimized structures indicated the absence of imaginary vibrational frequencies.

**Table S1.** Selected bond lengths (Å) and angles (°) for complexes **2** and **4** as determined crystallographically and optimized computationally.

| | **2** | | **4** | |
|---|---|---|---|---|
| | **X-Ray** | **DFT** | **X-Ray** | **DFT** |
| Co-B1 | 1.9463(13) | 1.954 | 1.9077(15) | 1.921 |
| Co-X[a] | 1.7745(13) | 1.771 | 2.1308(17) | 2.130 |
| Co-P1 | 2.1884(4) | 2.204 | 2.2422(5) | 2.265 |
| Co-P2 | 2.1901(3) | 2.204 | 2.2688(6) | 2.260 |
| P1-Co-P2 | 156.260(14) | 156.96 | 154.91(3) | 159.44 |

[a] X = N for **2**; X = B2 for **4**.

**Table S2.** Selected bond lengths (Å) and angles (°) for the four crystallographically independent molecules of complex **3** (donated as **3**, **3'**, **3''**, and **3'''**).

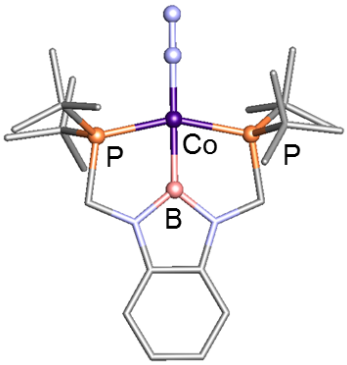
| | **3** | **3'** | **3''** | **3'''** |
|---|---|---|---|---|
| | **X-Ray** | **X-Ray** | **X-Ray** | **X-Ray** |
| Co-B1 | 1.922(4) | 1.893(4) | 1.915(5) | 1.901(5) |
| Co-P1 | 2.1936(12) | 2.2043(12) | 2.2006(12) | 2.1918(12) |
| Co-P2 | 2.1989(12) | 2.2118(13) | 2.2011(12) | 2.1933(12) |
| P1-Co-P2 | 152.61(5) | 154.48(5) | 153.16(5) | 154.16(5) |
| Out of plane distance for Co | 0.5612 | 0.4515 | 0.4962 | 0.2980 |

**Table S3.** Selected bond lengths (Å) and angles (°) for DFT-optimized isomers of complex **3**, namely boryl cobalt *trans*-dihydride dihydrogen (**A**), boryl cobalt *cis*-dihydride dihydrogen (**B**), dihydridoborato cobalt dihydrogen (**C**, the optimized structure is the same as **D**), and dihydridoborato cobalt dihydride (**D**).

| | **A** | **B** | **D** |
|---|---|---|---|
| | **DFT** | **DFT** | **DFT** |
| Co-B1 | 1.912 | 1.946 | 1.933 |
| Co-P1 | 2.210 | 2.205 | 2.210 |
| Co-P2 | 2.210 | 2.199 | 2.209 |
| P1-Co-P2 | 160.78 | 158.54 | 166.00 |

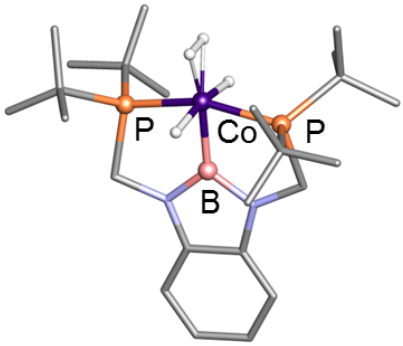
**DFT optimized structural coordinates**

Complex **2**



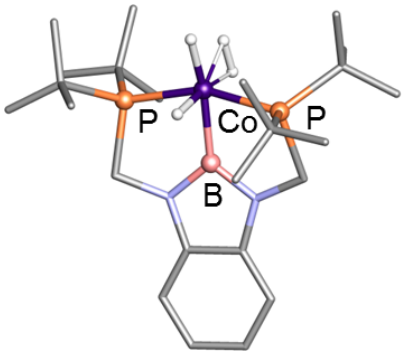

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Co | 0.000000 | -0.929000 | -0.000400 | C | -4.522600 | -0.515600 | 1.688000 |
| P | 2.158800 | -0.488900 | 0.052300 | H | -4.885600 | -0.537100 | 2.733400 |
| P | -2.158800 | -0.489000 | -0.052400 | H | -5.045100 | -1.320700 | 1.145700 |
| N | -1.131900 | 1.922600 | -0.180500 | H | -4.828600 | 0.453300 | 1.256200 |
| N | 1.131700 | 1.922700 | 0.180100 | C | -2.339300 | 0.339900 | 2.616200 |
| C | 2.447200 | 1.366600 | 0.410700 | H | -2.700800 | 0.172300 | 3.648600 |
| H | 2.782400 | 1.512100 | 1.455300 | H | -2.594600 | 1.377000 | 2.340500 |
| H | 3.219800 | 1.799300 | -0.253700 | H | -1.240000 | 0.247500 | 2.612600 |
| C | -2.447300 | 1.366400 | -0.411000 | C | -2.638900 | -2.113300 | 2.226300 |
| H | -2.782600 | 1.511700 | -1.455700 | H | -3.046300 | -2.218000 | 3.250200 |
| H | -3.219900 | 1.799100 | 0.253300 | H | -1.546700 | -2.255300 | 2.274700 |
| C | 0.710700 | 3.250400 | 0.117700 | H | -3.059300 | -2.927500 | 1.615500 |
| C | -1.413200 | 4.458400 | -0.239800 | C | 2.993500 | -0.709900 | -1.682600 |
| H | -2.492400 | 4.463400 | -0.425700 | C | 4.523300 | -0.515300 | -1.687100 |
| C | -0.711000 | 3.250400 | -0.118100 | H | 4.886700 | -0.536800 | -2.732400 |
| C | -0.695000 | 5.665800 | -0.118300 | H | 5.045900 | -1.320100 | -1.144400 |
| H | -1.227800 | 6.617900 | -0.209900 | H | 4.828900 | 0.453900 | -1.255500 |
| B | -0.000100 | 1.025000 | -0.000300 | C | 2.340100 | 0.339200 | -2.616400 |
| C | 0.694500 | 5.665900 | 0.118000 | H | 2.702300 | 0.171800 | -3.648600 |
| H | 1.227200 | 6.618000 | 0.209600 | H | 2.594400 | 1.376500 | -2.340700 |
| C | 1.412800 | 4.458600 | 0.239400 | H | 1.240800 | 0.246100 | -2.613600 |
| H | 2.492000 | 4.463600 | 0.425300 | C | 2.640400 | -2.113700 | -2.225800 |
| N | 0.000000 | -2.699700 | -0.000600 | H | 3.048000 | -2.218400 | -3.249500 |
| N | -0.000000 | -3.849500 | -0.000600 | H | 1.548300 | -2.256200 | -2.274300 |
| C | 3.196800 | -1.333400 | 1.450500 | H | 3.061100 | -2.927600 | -1.614800 |
| C | 2.303400 | -1.227800 | 2.712300 | C | -3.197300 | -1.333800 | -1.450000 |
| H | 2.807700 | -1.728400 | 3.561200 | C | -3.429600 | -2.825900 | -1.123600 |
| H | 1.323100 | -1.708400 | 2.551900 | H | -3.862500 | -3.325100 | -2.011300 |
| H | 2.119200 | -0.179400 | 3.005800 | H | -4.144300 | -2.960800 | -0.294300 |
| C | 4.558100 | -0.661800 | 1.747000 | H | -2.495400 | -3.351400 | -0.868900 |
| H | 5.031600 | -1.182300 | 2.601600 | C | -2.304300 | -1.228700 | -2.712100 |
| H | 4.455800 | 0.398000 | 2.034200 | H | -2.809200 | -1.729000 | -3.560800 |
| H | 5.257900 | -0.721200 | 0.899800 | H | -1.324200 | -1.709800 | -2.552100 |
| C | 3.428900 | -2.825600 | 1.124600 | H | -2.119800 | -0.180300 | -3.005700 |
| H | 3.861500 | -3.324700 | 2.012600 | C | -4.558600 | -0.662100 | -1.746100 |
| H | 4.143900 | -2.960800 | 0.295600 | H | -5.032800 | -1.183000 | -2.600200 |
| H | 2.494800 | -3.351000 | 0.869700 | H | -4.456100 | 0.397500 | -2.034100 |
| C | -2.992700 | -0.709700 | 1.683000 | H | -5.258000 | -0.720700 | -0.898500 |

Isomer **A**



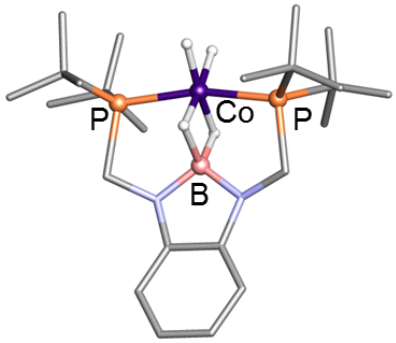

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Co | 0.003900 | -1.024600 | -0.016600 | H | -4.956100 | -0.636600 | 2.683200 |
| P | 2.179900 | -0.649400 | 0.062200 | H | -5.083800 | -1.514700 | 1.145400 |
| P | -2.175600 | -0.662900 | -0.062500 | H | -4.907700 | 0.268600 | 1.153700 |
| N | -1.139700 | 1.762900 | -0.220300 | C | -2.460400 | 0.286700 | 2.575700 |
| N | 1.129100 | 1.772400 | 0.159700 | H | -2.854800 | 0.150200 | 3.600300 |
| C | 2.426800 | 1.207700 | 0.456800 | H | -2.744600 | 1.299700 | 2.244500 |
| H | 2.702700 | 1.334400 | 1.522400 | H | -1.360900 | 0.232300 | 2.618500 |
| H | 3.239600 | 1.643900 | -0.155500 | C | -2.678900 | -2.193800 | 2.282600 |
| C | -2.439400 | 1.186300 | -0.483500 | H | -3.068700 | -2.246200 | 3.316900 |
| H | -2.736300 | 1.293400 | -1.545500 | H | -1.584400 | -2.321300 | 2.316800 |
| H | -3.242100 | 1.630000 | 0.136300 | H | -3.110400 | -3.038400 | 1.721100 |
| C | 0.696400 | 3.102500 | 0.108700 | C | 3.079000 | -0.834200 | -1.655300 |
| C | -1.427600 | 4.300200 | -0.268600 | C | 4.614000 | -0.675900 | -1.610100 |
| H | -2.504200 | 4.300900 | -0.470400 | H | 4.999600 | -0.662900 | -2.647200 |
| C | -0.722600 | 3.096700 | -0.146300 | H | 5.108800 | -1.514300 | -1.093200 |
| C | -0.718400 | 5.513800 | -0.125700 | H | 4.931600 | 0.268500 | -1.134400 |
| H | -1.257000 | 6.462700 | -0.217500 | C | 2.504000 | 0.261600 | -2.587000 |
| B | -0.001400 | 0.887000 | -0.032000 | H | 2.917700 | 0.112400 | -3.602000 |
| C | 0.664400 | 5.519400 | 0.131800 | H | 2.778300 | 1.280300 | -2.264700 |
| H | 1.192100 | 6.472700 | 0.241100 | H | 1.405700 | 0.202500 | -2.649500 |
| C | 1.387700 | 4.311600 | 0.251800 | C | 2.719800 | -2.213900 | -2.252600 |
| H | 2.464300 | 4.321000 | 0.453400 | H | 3.123100 | -2.281000 | -3.280900 |
| H | -0.016800 | -0.887200 | 1.485600 | H | 1.626300 | -2.344700 | -2.299700 |
| H | 0.022200 | -0.848900 | -1.515800 | H | 3.145900 | -3.049500 | -1.673500 |
| C | 3.227400 | -1.499200 | 1.457600 | C | -3.237500 | -1.539800 | -1.430800 |
| C | 2.405100 | -1.413000 | 2.766200 | C | -3.440300 | -3.025000 | -1.057400 |
| H | 2.993400 | -1.871500 | 3.583800 | H | -3.888200 | -3.559900 | -1.916000 |
| H | 1.443100 | -1.940200 | 2.679500 | H | -4.122000 | -3.151700 | -0.200100 |
| H | 2.185000 | -0.370800 | 3.055800 | H | -2.483700 | -3.520300 | -0.817800 |
| C | 4.596800 | -0.825600 | 1.721000 | C | -2.426300 | -1.473000 | -2.747500 |
| H | 5.082600 | -1.337100 | 2.573700 | H | -3.019500 | -1.946700 | -3.552800 |
| H | 4.492800 | 0.236000 | 2.002000 | H | -1.462100 | -1.995900 | -2.659200 |
| H | 5.285400 | -0.888000 | 0.867500 | H | -2.210600 | -0.435400 | -3.055900 |
| C | 3.438100 | -2.989800 | 1.110500 | C | -4.611800 | -0.875700 | -1.692300 |
| H | 3.881300 | -3.508700 | 1.981200 | H | -5.104800 | -1.405000 | -2.529800 |
| H | 4.126400 | -3.128600 | 0.260300 | H | -4.514600 | 0.180700 | -1.994600 |
| H | 2.484500 | -3.491700 | 0.872300 | H | -5.291000 | -0.924000 | -0.830300 |
| C | -3.048200 | -0.823700 | 1.669700 | H | -0.027400 | -2.567500 | 0.407500 |
| C | -4.583600 | -0.667200 | 1.641700 | H | 0.043600 | -2.553200 | -0.480600 |

Isomer **B**



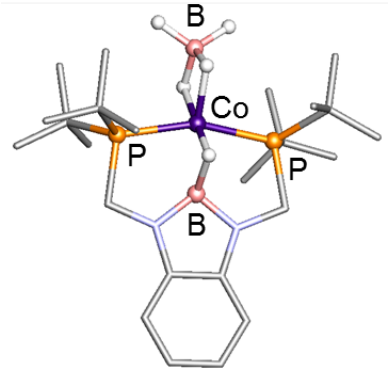

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Co | 0.035900 | -1.046300 | -0.155400 | C | 4.731600 | -0.630800 | -1.433900 |
| P | -2.142300 | -0.711400 | -0.079400 | H | 5.198700 | -0.667900 | -2.436700 |
| P | 2.182200 | -0.609300 | 0.043100 | H | 5.227000 | -1.399000 | -0.818700 |
| N | 1.092700 | 1.812400 | -0.082300 | H | 4.958700 | 0.361300 | -1.006900 |
| N | -1.178700 | 1.734800 | -0.451900 | C | 2.661600 | 0.095000 | -2.644300 |
| C | -2.483300 | 1.117400 | -0.572500 | H | 3.168600 | -0.102300 | -3.607600 |
| H | -2.875200 | 1.166200 | -1.607400 | H | 2.848600 | 1.149600 | -2.382300 |
| H | -3.235500 | 1.584600 | 0.091300 | H | 1.577500 | -0.025100 | -2.796500 |
| C | 2.378700 | 1.283400 | 0.322100 | C | 3.006600 | -2.332900 | -2.095800 |
| H | 2.582600 | 1.485300 | 1.392500 | H | 3.503500 | -2.440300 | -3.078600 |
| H | 3.224800 | 1.695900 | -0.261400 | H | 1.940400 | -2.572100 | -2.226200 |
| C | -0.816200 | 3.076300 | -0.288100 | H | 3.439900 | -3.086600 | -1.420200 |
| C | 1.244300 | 4.349000 | 0.183200 | C | -2.885600 | -0.794700 | 1.713700 |
| H | 2.321500 | 4.389900 | 0.377200 | C | -4.420800 | -0.634800 | 1.781200 |
| C | 0.603700 | 3.124400 | -0.043400 | H | -4.721500 | -0.557600 | 2.843200 |
| C | 0.469200 | 5.529500 | 0.160200 | H | -4.952800 | -1.502700 | 1.358800 |
| H | 0.956600 | 6.494000 | 0.336500 | H | -4.777600 | 0.279500 | 1.275400 |
| B | -0.005600 | 0.893100 | -0.310600 | C | -2.247800 | 0.359900 | 2.526600 |
| C | -0.915300 | 5.483200 | -0.086500 | H | -2.579400 | 0.274300 | 3.578400 |
| H | -1.494700 | 6.412100 | -0.102200 | H | -2.553800 | 1.355400 | 2.163700 |
| C | -1.573200 | 4.254700 | -0.315600 | H | -1.147300 | 0.313800 | 2.509900 |
| H | -2.651000 | 4.223900 | -0.508500 | C | -2.483000 | -2.135500 | 2.370300 |
| H | 0.091000 | -1.978900 | -1.387800 | H | -2.798800 | -2.125000 | 3.430900 |
| H | 0.014700 | -0.782700 | 1.282800 | H | -1.393500 | -2.289700 | 2.326000 |
| H | 0.043800 | -2.478600 | 0.389800 | H | -2.965400 | -3.000200 | 1.887100 |
| C | -3.282000 | -1.673100 | -1.324100 | C | 3.127100 | -1.339000 | 1.570000 |
| C | -2.567900 | -1.661100 | -2.698800 | C | 3.382000 | -2.845700 | 1.341600 |
| H | -3.244800 | -2.104300 | -3.453200 | H | 3.719700 | -3.306300 | 2.289200 |
| H | -1.644900 | -2.259800 | -2.685200 | H | 4.170400 | -3.025900 | 0.591700 |
| H | -2.312500 | -0.642400 | -3.038900 | H | 2.461700 | -3.363200 | 1.020400 |
| C | -4.682900 | -1.044000 | -1.523300 | C | 2.192800 | -1.187400 | 2.794700 |
| H | -5.234200 | -1.646300 | -2.270500 | H | 2.720800 | -1.564700 | 3.691000 |
| H | -4.629100 | -0.015500 | -1.918700 | H | 1.265700 | -1.765700 | 2.662600 |
| H | -5.288500 | -1.027800 | -0.606900 | H | 1.916200 | -0.136200 | 2.989800 |
| C | -3.425100 | -3.140800 | -0.864400 | C | 4.460100 | -0.622800 | 1.898000 |
| H | -3.897700 | -3.733200 | -1.670800 | H | 4.883500 | -1.071400 | 2.816900 |
| H | -4.063900 | -3.234600 | 0.029100 | H | 4.321300 | 0.452400 | 2.102400 |
| H | -2.442900 | -3.591200 | -0.640000 | H | 5.215900 | -0.726900 | 1.106900 |
| C | 3.215400 | -0.889200 | -1.582800 | H | 0.053900 | -1.095200 | -1.713500 |

Complex **3** (isomer **D**)




| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Co | 0.000200 | -0.937100 | 0.004900 | C | -4.539400 | -0.506600 | 1.789800 |
| P | 2.193200 | -0.669100 | 0.034000 | H | -4.944000 | -0.761900 | 2.787300 |
| P | -2.192800 | -0.669800 | 0.033900 | H | -5.247500 | -0.889900 | 1.041300 |
| N | -1.171700 | 1.826300 | -0.410800 | H | -4.526700 | 0.594700 | 1.721600 |
| N | 1.170700 | 1.826700 | -0.411800 | C | -2.257300 | -0.592100 | 2.826400 |
| C | 2.458800 | 1.245300 | -0.073400 | H | -2.749000 | -0.852600 | 3.782800 |
| H | 2.807500 | 1.606800 | 0.914300 | H | -2.141700 | 0.505600 | 2.800400 |
| H | 3.248700 | 1.483500 | -0.811000 | H | -1.251100 | -1.038700 | 2.809200 |
| C | -2.459500 | 1.244800 | -0.072100 | C | -3.214100 | -2.663200 | 1.780300 |
| H | -3.250300 | 1.483700 | -0.808600 | H | -3.550300 | -2.930100 | 2.799800 |
| H | -2.807200 | 1.605500 | 0.916300 | H | -2.231800 | -3.135900 | 1.609700 |
| C | 0.721300 | 3.145100 | -0.237000 | H | -3.941400 | -3.094100 | 1.072200 |
| C | -1.430800 | 4.340400 | -0.070000 | C | 3.122000 | -1.330200 | -1.532300 |
| H | -2.526100 | 4.344200 | -0.065900 | C | 4.643300 | -1.061300 | -1.538500 |
| C | -0.722500 | 3.144900 | -0.236500 | H | 5.044600 | -1.312800 | -2.538500 |
| C | -0.703300 | 5.540700 | 0.103000 | H | 5.180300 | -1.689600 | -0.809500 |
| H | -1.247000 | 6.481200 | 0.240000 | H | 4.895300 | -0.004500 | -1.342300 |
| B | -0.000500 | 0.958100 | -0.377400 | C | 2.482900 | -0.612400 | -2.747800 |
| C | 0.701500 | 5.541000 | 0.102600 | H | 2.968300 | -0.983000 | -3.669900 |
| H | 1.245000 | 6.481600 | 0.239300 | H | 2.614900 | 0.482800 | -2.721800 |
| C | 1.429200 | 4.340800 | -0.070900 | H | 1.405400 | -0.830600 | -2.817500 |
| H | 2.524500 | 4.345000 | -0.067400 | C | 2.862600 | -2.846100 | -1.684600 |
| H | -0.002800 | -1.953900 | 1.098200 | H | 3.240300 | -3.178800 | -2.670000 |
| H | 0.001400 | 0.205300 | 1.016600 | H | 1.783700 | -3.067800 | -1.631100 |
| H | -0.000200 | -2.190900 | -0.824100 | H | 3.379000 | -3.440700 | -0.914600 |
| C | 3.127700 | -1.123100 | 1.662200 | C | -3.121300 | -1.329900 | -1.532500 |
| C | 2.259100 | -0.587300 | 2.826300 | C | -2.862100 | -2.845800 | -1.685700 |
| H | 2.750500 | -0.847500 | 3.782900 | H | -3.246000 | -3.178800 | -2.668500 |
| H | 1.252200 | -1.032300 | 2.809800 | H | -3.372700 | -3.440800 | -0.912000 |
| H | 2.145100 | 0.510600 | 2.799000 | H | -1.782800 | -3.066700 | -1.638200 |
| C | 4.541000 | -0.507200 | 1.788200 | C | -2.482100 | -0.612300 | -2.748200 |
| H | 4.943700 | -0.756100 | 2.788100 | H | -2.966400 | -0.984300 | -3.670400 |
| H | 4.531300 | 0.593600 | 1.711700 | H | -1.404300 | -0.829200 | -2.817300 |
| H | 5.249400 | -0.897700 | 1.043700 | H | -2.615600 | 0.482600 | -2.723100 |
| C | 3.211700 | -2.661500 | 1.782900 | C | -4.642600 | -1.060700 | -1.538500 |
| H | 3.547500 | -2.927800 | 2.802700 | H | -5.043900 | -1.311300 | -2.538800 |
| H | 3.938000 | -3.095000 | 1.075300 | H | -4.894300 | -0.004100 | -1.341200 |
| H | 2.228500 | -3.132400 | 1.613100 | H | -5.179500 | -1.689800 | -0.810100 |
| C | -3.127100 | -1.124800 | 1.661800 | H | 0.000500 | -0.105300 | -1.301800 |

Complex **4**




| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Co | -0.011700 | -0.976300 | -0.171200 | H | -3.639900 | -2.885800 | -2.750000 |
| P | -2.235900 | -0.577100 | -0.014200 | H | -3.668500 | -3.198400 | -0.996700 |
| P | 2.216400 | -0.616000 | -0.053900 | H | -2.110400 | -2.965900 | -1.824600 |
| N | -1.121300 | 1.851300 | -0.057300 | C | -3.258300 | -1.100500 | -1.576300 |
| N | 1.175400 | 1.823600 | -0.167300 | C | -4.744600 | -0.685600 | -1.529700 |
| C | -0.675200 | 3.173400 | -0.071700 | H | -5.196300 | -0.859100 | -2.525000 |
| C | -2.465400 | 1.328500 | -0.001800 | H | -4.889000 | 0.381500 | -1.287400 |
| H | -3.085600 | 1.663600 | -0.855600 | H | -5.317200 | -1.288200 | -0.806700 |
| H | -2.985500 | 1.635400 | 0.924000 | C | -2.573800 | -0.406900 | -2.781300 |
| C | 0.763300 | 3.156200 | -0.154200 | H | -3.099000 | -0.708500 | -3.706900 |
| C | -0.630200 | 5.588900 | -0.066400 | H | -1.518000 | -0.710400 | -2.872300 |
| H | -1.159600 | 6.546600 | -0.032800 | H | -2.611100 | 0.694600 | -2.726000 |
| C | 1.487900 | 4.354900 | -0.198600 | C | 4.684100 | -0.683500 | -1.651200 |
| H | 2.580800 | 4.347700 | -0.268200 | H | 5.213200 | -1.188200 | -2.482000 |
| C | 0.774600 | 5.572400 | -0.154200 | H | 5.346500 | -0.717800 | -0.773900 |
| H | 1.326200 | 6.517500 | -0.189500 | H | 4.557500 | 0.371300 | -1.947100 |
| C | -1.371800 | 4.388300 | -0.023200 | C | 3.336200 | -1.409200 | -1.421900 |
| H | -2.464900 | 4.405900 | 0.039900 | C | 2.504400 | -1.319600 | -2.725400 |
| B | 0.015200 | 0.943200 | -0.109900 | H | 3.090000 | -1.756900 | -3.556200 |
| B | -0.009600 | -3.077800 | 0.176200 | H | 2.265800 | -0.276700 | -3.000100 |
| C | 2.483600 | 1.249700 | -0.379000 | H | 1.555500 | -1.871500 | -2.635300 |
| H | 3.249200 | 1.661400 | 0.305500 | C | 3.608400 | -2.896000 | -1.104600 |
| H | 2.839900 | 1.411700 | -1.414900 | H | 4.080900 | -3.369500 | -1.986200 |
| H | -0.014800 | 0.004600 | -1.298000 | H | 2.681000 | -3.445000 | -0.875500 |
| H | -0.018000 | -2.481600 | -0.976800 | H | 4.305200 | -3.016400 | -0.258000 |
| H | -0.023100 | -2.098700 | 1.067600 | C | 4.506300 | -0.481600 | 1.754100 |
| C | -3.140400 | -1.050500 | 1.639200 | H | 4.831800 | -0.456200 | 2.811300 |
| C | -4.505600 | -0.350400 | 1.853500 | H | 4.750900 | 0.501300 | 1.316200 |
| H | -4.900100 | -0.669900 | 2.836600 | H | 5.111500 | -1.250400 | 1.247100 |
| H | -5.254000 | -0.628100 | 1.096800 | C | 2.997700 | -0.811300 | 1.711500 |
| H | -4.435000 | 0.749600 | 1.882800 | C | 2.786300 | -2.238300 | 2.262800 |
| C | -3.359000 | -2.576300 | 1.738100 | H | 3.182900 | -2.275400 | 3.295200 |
| H | -3.688600 | -2.821200 | 2.765700 | H | 3.313100 | -3.004700 | 1.673700 |
| H | -2.440200 | -3.143800 | 1.525400 | H | 1.722200 | -2.513500 | 2.292900 |
| H | -4.150300 | -2.922200 | 1.051600 | C | 2.229900 | 0.178100 | 2.623300 |
| C | -2.181000 | -0.600900 | 2.769600 | H | 2.580200 | 0.045300 | 3.664200 |
| H | -2.654400 | -0.816900 | 3.746000 | H | 1.144400 | -0.011800 | 2.593300 |
| H | -1.966000 | 0.481700 | 2.734900 | H | 2.395200 | 1.232900 | 2.347500 |
| H | -1.220800 | -1.138000 | 2.722700 | H | -1.016100 | -3.742000 | 0.308100 |
| C | -3.157500 | -2.628100 | -1.788000 | H | 1.004100 | -3.725300 | 0.334100 |

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